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THE ELECTRONIC STRUCTURE OF SQUARE-PLANAR NICKEL(II) AND COPPER(II) COMPLEXES

A THESIS

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THE ELECTRONIC STRUCTURE OF SQUARE-PLANAR

NICKEL(II) AND COPPER(II) COMPLEXES

Approved:

Chairman

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SUMMARY

The electronic structure of square-planar copper(II) and nickel(II) complexes has been studied using spectral and magnetic methods. The study has concentrated attention on complexes using a simple saturated amine, 1,5-diazocyclooctane, as the ligand and then the results have been related to more complicated systems.

The bis(DACO)copper(II) perchlorate dihydrate was found to have a $^2B_{1g}$ ground state. The excited states, $^2B_{2g}$, ^2E_g, and $^2A_{1g}$, are found to be at 18.2, 20.8, and 23.8 kK above the ground state. This order corresponds to the d orbitals having an energy order $d_{x^2-y^2} > d_{xy} > d_{xz}$, $d_{yz} > d_{z^2}$ just as predicted by crystal field theory for complexes with no z axis interaction.

The bis(DACO)nickel(II) perchlorate dihydrate complex is found to have a $^1A_{1g}$ ground state. The excited states $^1B_{1g}$, $^1A_{2g}$, and ^1E_g excited states are found to be 23.7, 22.3, and 21.6 kK above the ground state. Ligand field calculations indicate that the three excited states are of very nearly the same energy. Because of the resemblance of solution and solid state spectra of other square-planar amine complexes, the electronic structure of these complexes must be very nearly the same as that assigned above. The one absorption band observed in the visible spectra of these complexes must therefore correspond to electronic transitions from the ground state to the three excited states.

Several other conclusions were made. Because of the order of the levels and the relatively small shift of the absorption band in various solvents, the

electron-electron interaction must be very important in the nickel(II) complexes. Because of the relatively high temperature independent paramagnetism of the nickel(II) complexes, there must be considerable mixing between triplet and singlet states. The best description of the square-planar complexes is that there is a relatively strong interaction with the $d_{x^2-y^2}$ and the other levels are only influenced by the electrostatics of the field.

CHAPTER I

INTRODUCTION

The nature of the electronic structure of octahedral complexes of transition metal complexes is now fairly well understood. On the other hand, the analysis is less complete for square-planar or highly tetragonal complexes.

The theoretical analysis of the square-planar complexes has been along the lines of the ligand field (1) and molecular orbital (2) approaches. Gray (2) has used the molecular orbital approach to derive a general energy level diagram for the square-planar transitional metal complexes. The crystal field approach by Maki (1) is specifically for the nickel(II) ion. The crystal field approach for the copper(II) ion is not complicated and has been given by many authors (3, 4).

Let us briefly examine the results of the above mentioned work. The convention of Gray (2) that the metal ion is positioned at the center of the cartesian coordinate system will be used. The four ligand donor atoms in the $\underline{xy}$ plane are located on the $\underline{x}$ and $\underline{y}$ axes as shown in Figure 1.

In the crystal field approach, the ligands are considered to be point charges or dipoles. The ligand field due to the point charges or dipoles splits the degenerate subshell into four states. In ligand fields of D_{4h} symmetry the $\underline{d}_{x^2-y^2}$ orbital of b_{1g} symmetry has its lobes directed towards the ligands and is less stable because of the electrostatic effects. The $\underline{d}_{xy}$ orbital of b_{2g} symmetry has its lobes in the same plane but between the ligands, while the $\underline{d}_{xz}$ and $\underline{d}_{yz}$ orbitals of e_g symmetry

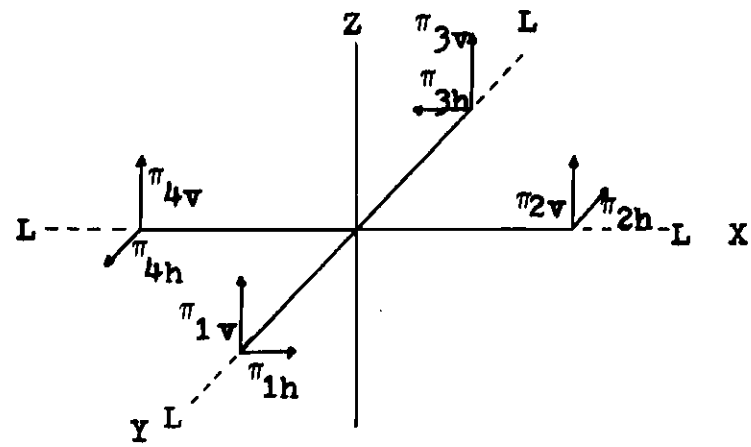

Figure 1. The Definition of the Geometry of Square Planar Complexes.

are located above and below the plane. The $\underline{d}_{z^2}$ orbital of a_{1g} symmetry has its large lobe directed along the $\underline{z}$ axis with a smaller lobe in the $\underline{xy}$ plane. On the basis of purely electrostatic interactions the order of the energy levels is $b_{1g} > b_{2g} > e_g$ with the a_{1g} level being lower than the b_{1g} but its position relative to the b_{2g} and e_g levels being uncertain. If the interaction with the lobe in the $\underline{xy}$ plane is small then the a_{1g} level should be of lowest energy.

Divalent copper has the electronic configuration of the argon subshell plus nine 3 $\underline{d}$ electrons. The free ion has a ^2D ground state. Imposing an electrostatic field composed of negative ions or dipoles with negative ends pointing at the central metal atom all of whose orbitals except one are filled is equivalent to the case where one positron occupies the same orbitals. Through this thesis, the convention will be used that the $\underline{d}^8$ and $\underline{d}^9$ subshell will be treated as the much simpler two and one positron case. The arguments made above for the $\underline{d}$ orbitals are entirely analogous to those for the ^2D state (4). Then depending upon the degree of

electrostatic interaction with the $^2A_{1g}$ state the following possible energy state sequences of the copper(II) ion may arise:

a) $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$

b) $^2B_{1g} < {}^2B_{2g} < {}^2A_{1g} < {}^2E_g$

c) $^2B_{1g} < {}^2B_{2g} < {}^2E_g < {}^2A_{1g}$

Divalent nickel has the electronic configuration of [A] $(3d)^8$ and has a ^3F ground state with ^1D, ^1G, ^1S and ^3P excited states. Imposing a square-planar field on the central ion will remove some of the degeneracy of the free ion states. According to the "weak field" approach (1) the ^3F ground state will be split into $^3A_{2g}$, $^3B_{1g}$, $^3B_{2g}$ and two ^3E_g states; the ^1D state into $^1A_{1g}$, $^1B_{1g}$, ^1E_g, and $^1B_{2g}$ states; the ^3P into $^3A_{2g}$ and ^3E_g; the ^1G into two $^1A_{1g}$ states, two ^1E_g states, one $^1A_{2g}$ state, one $^1B_{1g}$ state and one $^1B_{2g}$ state while the ^1S will be unsplit. The calculation of the energy of these levels relative to the free ion ground state was made using the effective interelectron distance, dipole moment and point charges as parameters. The interelectron distance is defined as the distance from the effective location of the electron pair of the ligand to the effective location of the d subshell. The results reveal that at relatively short interelectron distances, high dipole moments and point charges, the ground state becomes a singlet ground state, but no conclusions could be reached as to the energy of the excited singlet states. This is true because the energy of the excited states relative to the ground state is highly dependent on the values of the parameters.

Another theoretical approach to the electronic structure is the molecular orbital approach as outlined by Gray (2). Each ligand is assumed to have a valence orbital directed towards the metal. The ligand may also have two equivalent valence orbitals which are parallel (π_h orbital) and perpendicular (π_u orbital) to the plane. The transition metal is assumed to have the usual nine valence orbitals; five 3d's, one 4s, and three 4 p's. The metal orbitals used in forming σ molecular orbitals are the 3 $d_{x^2-y^2}$, $4p_x$, $4p_y$ and a combination of the 3 d_{z^2} and 4s. The metal orbitals used in π bonding are divided into three groups. The "in-plane" π bonding occurs through the d_{xy} and four π_u ligand orbitals, the "trans" π bonding occurs through the $3d_{xz}$ and $3d_{yz}$ with the π ligand orbitals and the "ring" π system bonds through the $4p_z$ orbital with the four π ligand orbitals. In addition to the three major π systems, the $4p_x$ and $4p_y$ orbitals each interact with two π orbitals. The energy level scheme according to Gray is given in Figure 2. The stable levels will be mainly located on the ligand and these are the σ and π bonding levels. The molecular orbitals derived from the metal d orbitals are found at higher energy. The exact ordering of these levels is not known and the order given reflects the views of Gray (2) concerning the square-planar halides and cyanides.

The molecular orbital diagram shown in Figure 2 is a general diagram for square-planar complexes of transition metal complexes. In the case of nickel(II) the ground state has all levels filled until the $d_{x^2-y^2}$ where one electron resides. According to this diagram three types of transitions to excited states may occur; the d to d transitions which are spin-allowed, Laporte forbidden, and of relatively low intensity; and the Laporte allowed "charge transfer" transitions which may be from the ligand bonding orbitals to the d orbitals or from the d orbitals to the

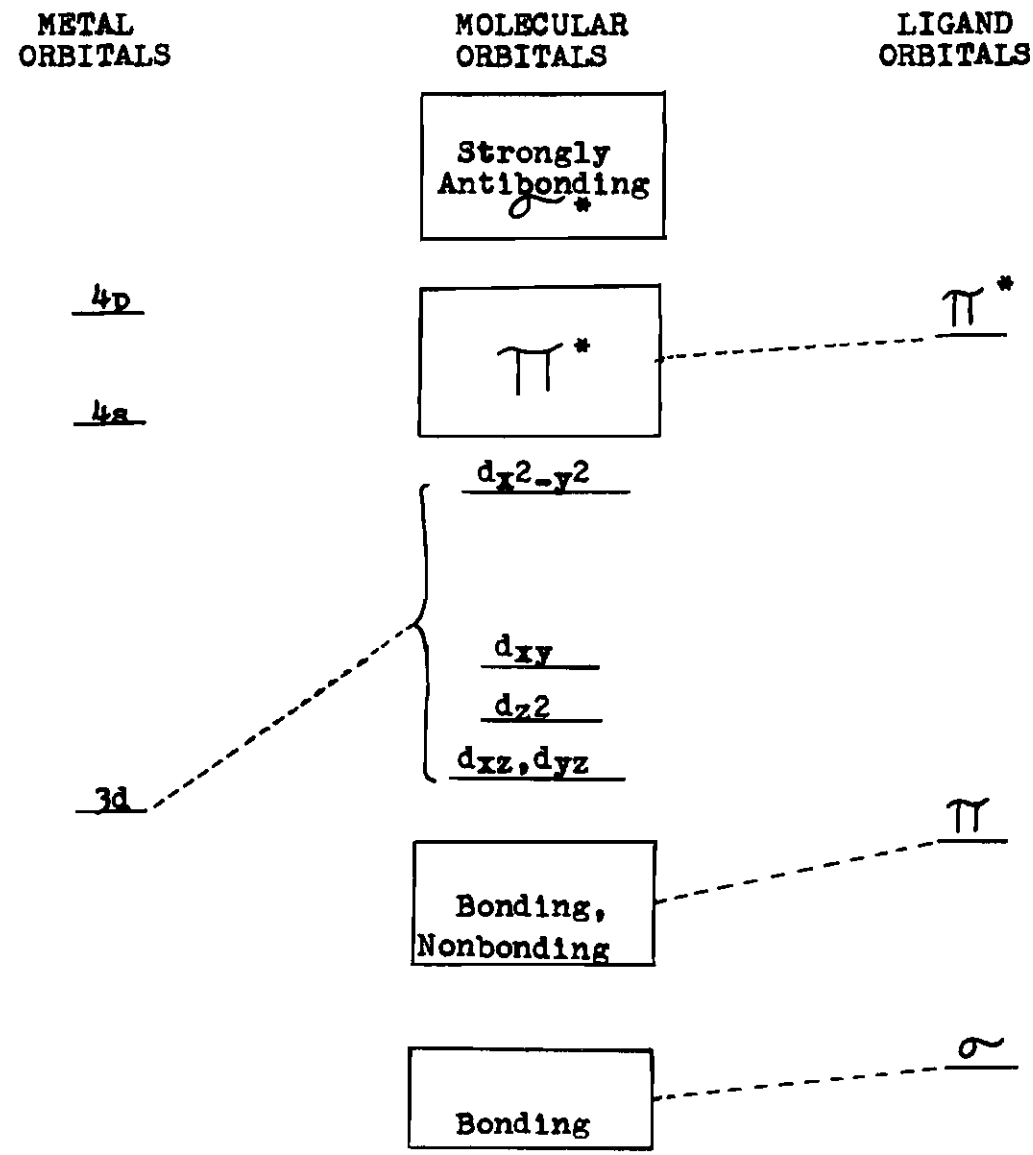

Figure 2. Simple Energy Level Scheme for Square-planar Complexes. (The diagram is only an attempt to show the types of transitions that may occur. The broken lines are an attempt to correlate the molecular orbitals to the orgin of their dominate character. The $d_{x^2-y^2}$ molecular orbital is really a σ^* orbital, while all of the other d orbitals may be π^*.)

ligand antibonding orbitals (4). The reason that one speaks of the molecular orbitals as being either ligand or metal orbitals is that a great deal of mixing of the component atomic orbitals is not expected. This fact may be appreciated by examining the electroneutrality principle. If one starts with a free metal ion of charge 2 + one expects that the ligand system would transfer two electrons to the metal ion. If a set of σ-type bond molecular orbitals contain more than 25 per cent participation of the electrons of the ligand, the charge on the metal ion would become negative. Consequently the metal orbitals remain mostly metal orbitals, and the ligand orbitals remain mostly ligand orbitals in the complex.

Our approach to the problem of determining the electronic structure of planar complexes is to start with the most simple cases and then make extensions to more complicated systems. The most obvious simplification is to have the highest symmetry of the ligand field possible and that is D_{4h}. Lower symmetry will remove the degeneracy of the E_g states and increase the number of transitions by one. From the molecular orbital approach we see that there are several ways of simplifying the electronic spectra. If ligand systems are used which retain their electrons very strongly, the d orbitals will remain essentially pure d orbitals in the complex. Furthermore, if ligand systems are used which have no atomic orbitals or molecular orbitals capabile of forming π or π^* type molecular orbitals in the complex, only the σ interaction need be considered in the molecular orbital approach. Such a system could be explained in terms of a modification of crystal field theory known as ligand field theory.

At the time of the undertaking of this study there were no ligand systems

known which met the above description. The square-planar complexes of salicylaldiminate (5, 6) anion could certainly not be classified as having D_{4h} symmetry. The four coordinate systems containing phosphorous (7) and sulfur (8) are complicated by the fact that there may be mixing with the low-lying empty d levels of the ligands. Quinoline and pyridine heterocyclic ring systems often yield complexes of square-planar structure (9) but these systems are complicated by possible interaction with the π electron systems. Porphyrins (10) and phthalocyanines (11) have a high degree of conjugation and are also undesirable for the same reason.

Square-planar complexes composed of saturated amine ligands where there is no conjugation or resonance are ideal systems for our study. The problem, though, is that coordination with most amines does not stop at four but proceeds to octahedral or six coordination. Limiting the ratio of amine to metal in the reaction solution to the proper ratio for four coordination may produce a product that has the correct amine to metal ratio, but then the other two positions of the octahedron or distorted octahedron may be occupied by solvent molecules, anions or coordinated metal atom (that is, a metal to metal interaction). The way that interaction along the z axis is prevented is by blocking the z axial positions with non-coordinating methyl or methylene group of saturated amines. We must require that nonbonding interaction of these groups with similar groups within the ligand or other ligands coordinated to the central metal ion be minimal. If such an interaction is great in our models, then the complexes are expected not to be stable or to undergo some type of distortion and lower the ligand field symmetry from D_{4h}.

The model studies revealed that a satisfactory system is that of bis(1, 5-

diazacyclooctane) nickel(II) and copper(II) perchlorate. The perchlorate anion was chosen since it is known to have very little tendency to coordinate as compared to the halides and nitrates. At the time of undertaking of this study the above mentioned complexes had not been reported. Musker and Hussian (9) published the preparation and some of the characteristics of these compounds several months after we began work on the preparation and their work confirmed our predictions of a square-planar structure.

In our study the following approach was used. First a series of complexes which are believed to be four coordinate were prepared. These were characterized using standard chemical, spectral, and magnetic analyses. The solution and solid spectra of these complexes were investigated in hopes that shifts in bands indicative of solvent interaction would be observed. Single crystal polarized spectra were investigated with the hope that additional assignments could be made. Finally, the magnetic properties were examined as a function of temperature with the hope that the nature of the ground state might be understood.

Another portion of the study outlined in Chaper IV is concerned with a ligand field calculation for the square-planar nickel(II) complex. In this calculation Maki's (1) crystal field approach is modified by making allowance for some covalent bonding and that the parameters are related to the observed spectra of the copper(II) complex. In Chapter V the phases of the studies are organized and conclusions are made as to the nature of the electronic structures of the square-planar nickel(II) and copper(II) complexes.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes

1,5-Diazocyclooctane

Two methods for the preparation of 1,5-diazacyclooctane (DACO) have been reported in the literature (13, 14).

Terent'ev, Kost, and Chursina have prepared DACO by the reaction of 1,3-propanediamine with acrylonitrile followed by reduction. Acrylonitrile (53.0g) was slowly added to 76.0 g of 1,3-propanediamine. The temperature was maintained at 40 to 45° during the addition and the solution was then heated for two hours at 100°. The solution was rapidly distilled under reduced pressure (approximately 25 mm) and the fraction containing $H_2N(CH_2)_3$ NH-CH_2 CH_2CN boiling at 115° C was collected. This fraction was reduced with a solution of 75 g of sodium in 1250 mls of n-butyl alcohol. Steam distillation produced a mixture of water, n-butyl alcohol, and DACO. Addition of hydrochloric acid and drying by means of a rotatory vacuum system produce impure DACO·2HCl in low yield.

Buhle, Moore, and Wiseloge (14) report that DACO can be prepared by the reaction of hydrazine and 1, 3-dibromopropane in an 95% ethanol solution followed by reduction. A 33.4 g sample of 95% hydrazine and 250 ml of 95% ethanol were placed in a 2 liter, 3 necked flask provided with a mechanical stirrer, reflux condenser and dropping funnel. A 101 g portion of 1,3-dibromopropane was added to

the gently refluxing solution over a period of 2.5 hours. The mixture was cooled at 0° for several hours and the crystalline hydrazine monohydrobromide was filtered off. The solution was acidified with hydrobromic acid and treated with 50 ml of benzaldehyde. The crystalline benzaldazine was filtered and the filtrate, diluted with 200 mls of water, was extracted with 200 mls of ether. Removal of the solvent from the aqueous layer left a residue of salt. Digestion with absolute alcohol left the DACO·2HBr.

We attempted to use the method of Terent'ev, Kost, and Chursina (13), but found that the yield was extremely low. Although the method of Buhle, Moore, and Wiseloge also gave a low yield, it was much quicker, required less labor, and did not require any reduction using sodium metal. Hence the latter method was used to prepare a large percentage of the DACO·HBr used. The pure amine was produced by the treatment of a saturated solution of DACO·2HBr with sodium hydroxide. The DACO layer was removed and distilled under vacuum. The decomposition point of DACO·2HCl agreed with the one reported by Terent'ev, Kost and Chursine (250° as compared to a reported value of 270°).

Bis (1,5-Diazocyclooctane) Nickel(II) and Copper(II) Perchlorate

The hydrated complexes were prepared by mixing 95% ethanol solutions containing 2:1 stoichiometric quantities of the amine and the metal perchlorate. The precipitated complexes were isolated by filtration, washed with 95% ethanol, recrystallized from 95% ethanol, and dried in a desiccator. The anhydrous complexes were prepared by heating hydrous complexes at 100° under a high vacuum. The infrared and visible spectra absorption spectra agreed with those reported by

Musker and Hussain (12).

The gravimetric analysis of $[Ni(DACO)_2(H_2O_2]](ClO_4)_2$ using dimethylglyoxime indicates 11.5% nickel as compared to a calculated value of 11.3%. Electrolysis of acid solutions of the copper complex indicates 12.4% copper as compared to a calculated value of 12.1%.

1,5,9,13-Tetraaza-2,4,4,10,12,12-hexamethylcyclohexadeca-1,9-dienenickel(II) Perchlorate ($NiTAHD(ClO_4)_2$)

The procedure followed was one outlined by Curtis and coworkers (15). Tris-(1,3-propanediamine) nickel(II) perchlorate (20 g) was dissolved in acetone (100 mls) and allowed to stand at room temperature in a stoppered flask. After several days, orange crystals of $[Ni(TAHD)](ClO_4)_2$ were formed on the walls of the flask. After a week, the solution was decanted and the solid was washed with hot ethanol. Recrystallization from hot water gave orange crystals of $[Ni(TAHD)](ClO_4)_2$ which were dried in a vacuum desiccator. Analysis of the complex indicated 9.9% nickel as compared to calculated 10.4%. The visible and ultraviolet spectra agree with those reported by House and Curtis (16). The infrared spectra indicates the absence of the broad transition characteristic of water and the presence of absorbance indicative of perchlorates with T_d symmetry (17). This indicates that the perchlorates are not coordinating.

1,5,9,13-Tetraaza-2,4,4,10,12,12-hexamethylcyclohexadecanenickel(II) Perchlorate ($Ni(TAH)(ClO_4)_2$)

Approximately 10 g of $Ni(TAHD)(ClO_4)_2$ and 0.3 g of platinum oxide (Adam's catalyst) were suspended in water. The suspension was treated with hydrogen in

an autoclave at 5,000 lbs/in^2 at room temperature. The suspension was removed from the autoclave, heated to boiling, the catalyst filtered off, and the solution cooled. The maroon precipitate was filtered off and dried in a vacuum desiccator. The infrared absorption spectra indicates the absence of water and coordinating perchlorate anions. Elemental analysis agrees with the stoichiometry Ni(TAH)$(ClO_4)_2$. Calculated: Ni, 10.30%; C, 38.05%; H, 6.47%; N, 9.86%. Found: Ni, 10.30%; C, 38.04%; H, 6.79%; N, 9.63%.

5,5,7,12,12,14, Hexamethyl - 1,4,8,11-tetraazocyclotetradeca - 1,8-diene-nickel(II) Perchlorate (Ni(CTA)$(ClO_4)_2$) and 5,7,7,12,14,14-Hexamethyl-1,4,8,11 - tetrazocyclotetradeca - 1,5-dienenickel(II) Perchlorate (Ni(CTB)$(ClO_4)_2$)

Preparation of the complexes has been reported in the literature by Curtis and coworkers (15). One hundred grams of trisdiaminoethanenickel(II) perchlorate was dissolved in 500 mls of acetone and allowed to react in a stoppered flask over a two week period. The tarry liquid was decanted from the orange solid and the solid was washed several times with hot ethanol. The two isomers were separated by taking advantage of the greater solubility of Ni(CTA)$(ClO_4)_2$ in hot water. Purity of the two isomers was indicated by the agreement of the infrared spectra with that reported by Curtis and coworkers (15).

5,7,7,12,14,14 - Hexamethyl - 1,4,8,11 - tetraazocyclotetradecanenickel(II) Perchlorate (Ni(HTTA)$ClO_4)_2$)

The preparation of Ni(CTA)$(ClO_4)_2$ has been reported in the literature by Curtis (15). Five grams of Ni(CTA)$(ClO_4)_2$ and 0.1 g of Adams catalyst were suspended in 150 mls of water. The suspension was treated in an autoclave with

hydrogen at 5000 lbs/in^2 for three days. The suspension was removed from the autoclave and heated to boiling. The catalyst was filtered off while the solution was hot and then the Ni (HTTA)$(ClO_4)_2$ was allowed to precipitate while the solution cooled. The solid was filtered off and dried under vacuum. The infrared spectra indicated that no water is present, the C=N bonds have been completely hydrogenated and that perchlorate groups are not coordinating. The visible spectra and magnetic data are in agreement with Curtis's (15) data.

5, 7, 7, 12, 12, 14 - Hexamethyl - 1, 4, 8, 11-tetraazocyclotetradecanenickel(II) Perchlorate (Ni(HTTB)$(ClO_4)_2$)

The method of preparation for Ni(HTTB)$(ClO_4)_2$ is essentially the same as for Ni(HTTA)$(ClO_4)_2$ except that Ni(CTB)$(ClO_4)_2$ was substituted for Ni(CTA) $(ClO_4)_2$.

Bis-acetylacetonatecopper(II)

The complex was prepared by treating an aqueous solution of copper(II) chloride with an excess of 2, 4-pentanedione. The steel blue precipitate was filtered off, washed with ethanol and then recrystallized from hot ethanol. Visible spectra of solutions agreed with those reported by Belford, Calvin, and Belford (18).

Spectra

Infrared Spectra

All infrared spectra were obtained using nujol mulls with sodium chloride plates. The instruments used were the Perkin Elmer Infracord or 457.

Visible, Near Infrared and Ultraviolet Solution Spectra

The visible spectra were recorded using a Cary 14 or a Beckman DK-1. The majority of solution spectra for the copper(II) complex were obtained on the DK because the range of interest could be obtained without changing detectors or the light source. On the other hand, the solution spectra for the nickel(II) complexes were obtained using the Cary 14 for the same reason. The two instruments produced spectral data that agreed very well. The UV spectra were obtained using the instruments indiscriminately.

One-centimeter matched quartz cells were used in all cases. The base line using the above mentioned cells filled with the appropriate solvent were always determined and the resulting absorption curves reflect the difference of absorption due to the complex ions. Care was taken to avoid frequencies at which the solvent absorbs appreciably. The results of some of the measurements are shown in Figures 3 through 8.

Single Crystal Visible Spectra

With the exception of bis(acetylacetonate) copper(II), single crystals of all complexes prepared were visually examined using a microscope equipped with an optical polarizer. Of all those examined, only bis(DACO) nickel(II) and bis(DACO) copper(II) perchlorates dihydrates appeared to be dichroic. Furthermore, the crystals are so similar that the ensuing discussion applies to crystals of both complexes. The crystalline habits of both of these complexes are orthorhombic with not very well defined ends or edges. The crystallographic axes are always found to be parallel to the rectangular edges. The rectangular faces of the crystals

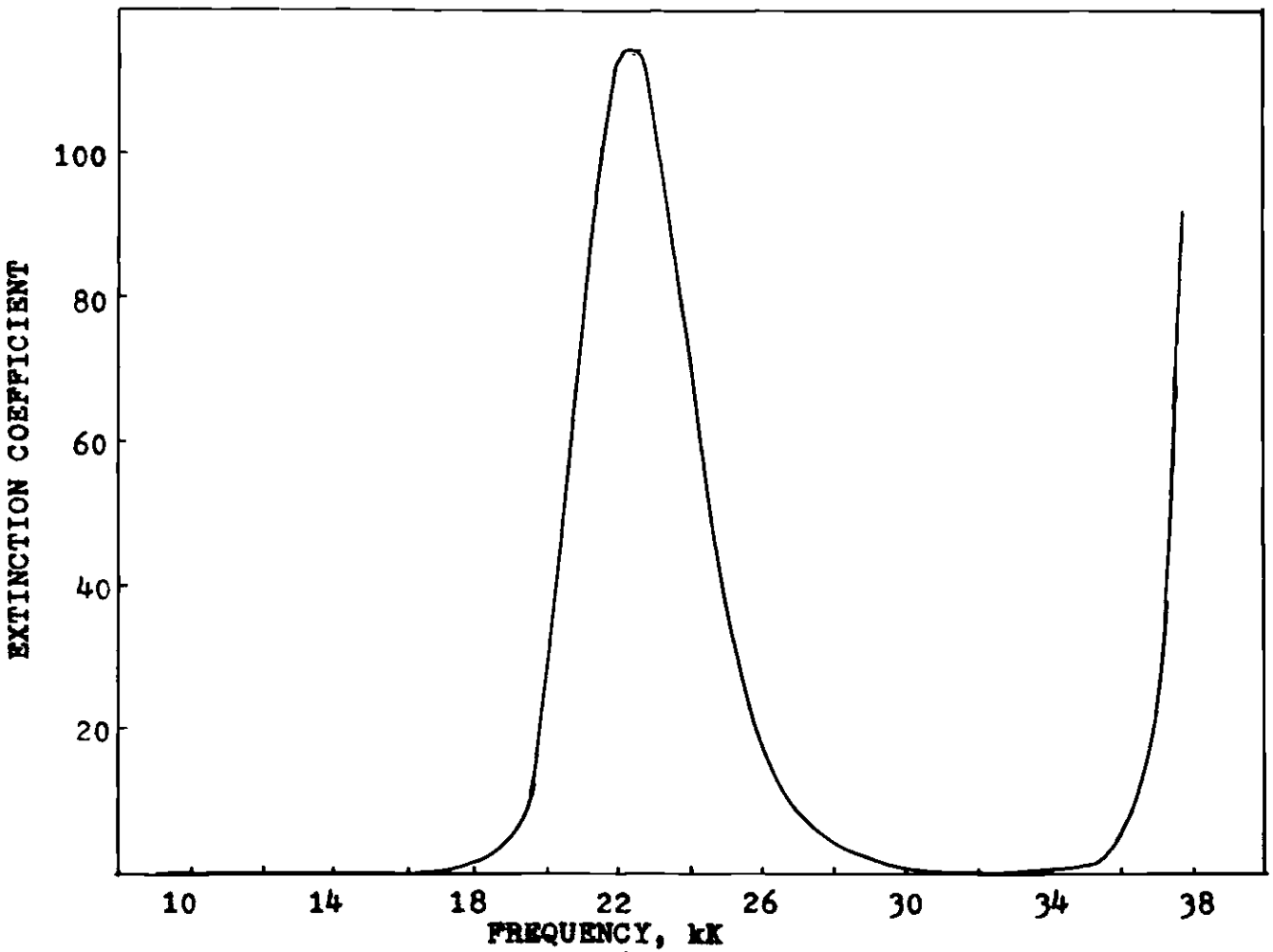

Figure 3. The Spectrum of bis(1,5 Diazacyclooctane)nickel(II) Perchlorate in Water.

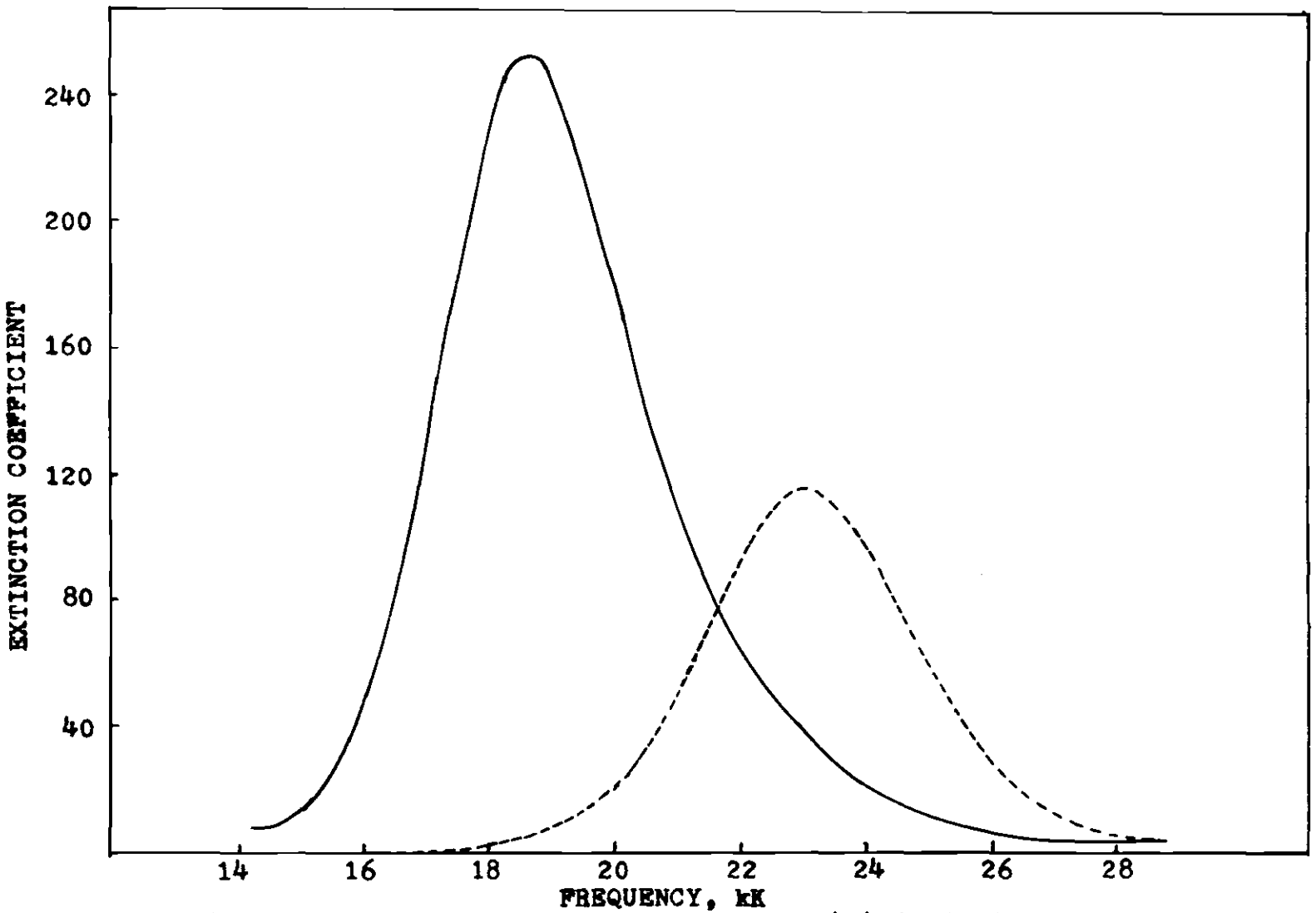

Figure 4. The Spectrum of 1,5,9,13-Tetraaza-2,4,4,10,12,12-hexamethylcyclohexadeca-1,9-dienenickel(II) Perchlorate (the broken line) and 1,5,9,13-Tetraaza-2,4,4,10,12,12-hexamethylcyclohexadecanenickel(II) Perchlorate (the solid line) in DMSO.

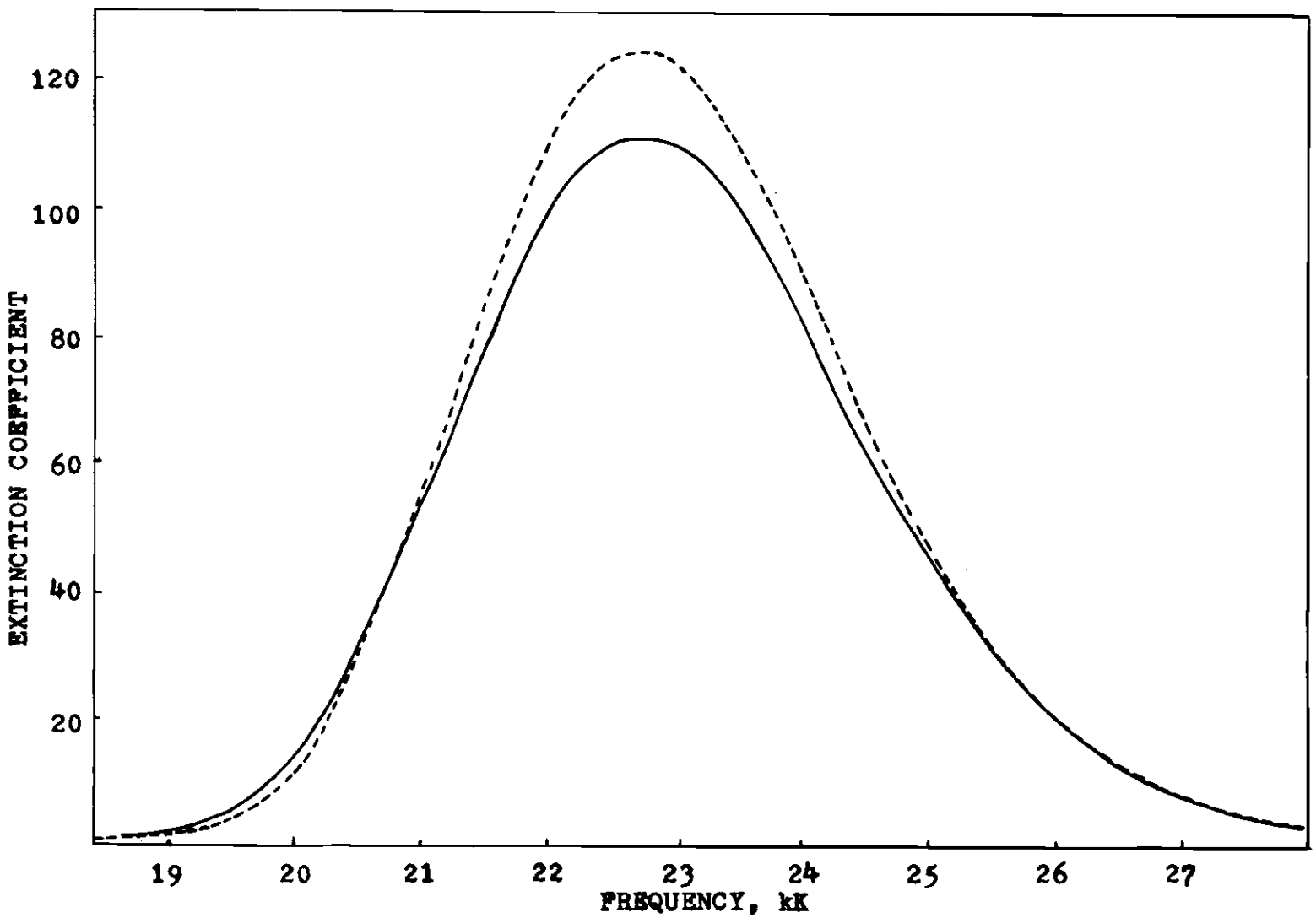

Figure 5. The Spectrum of cis (the broken line) and trans (the solid line) Isomers of Hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II) Perchlorate in Water.

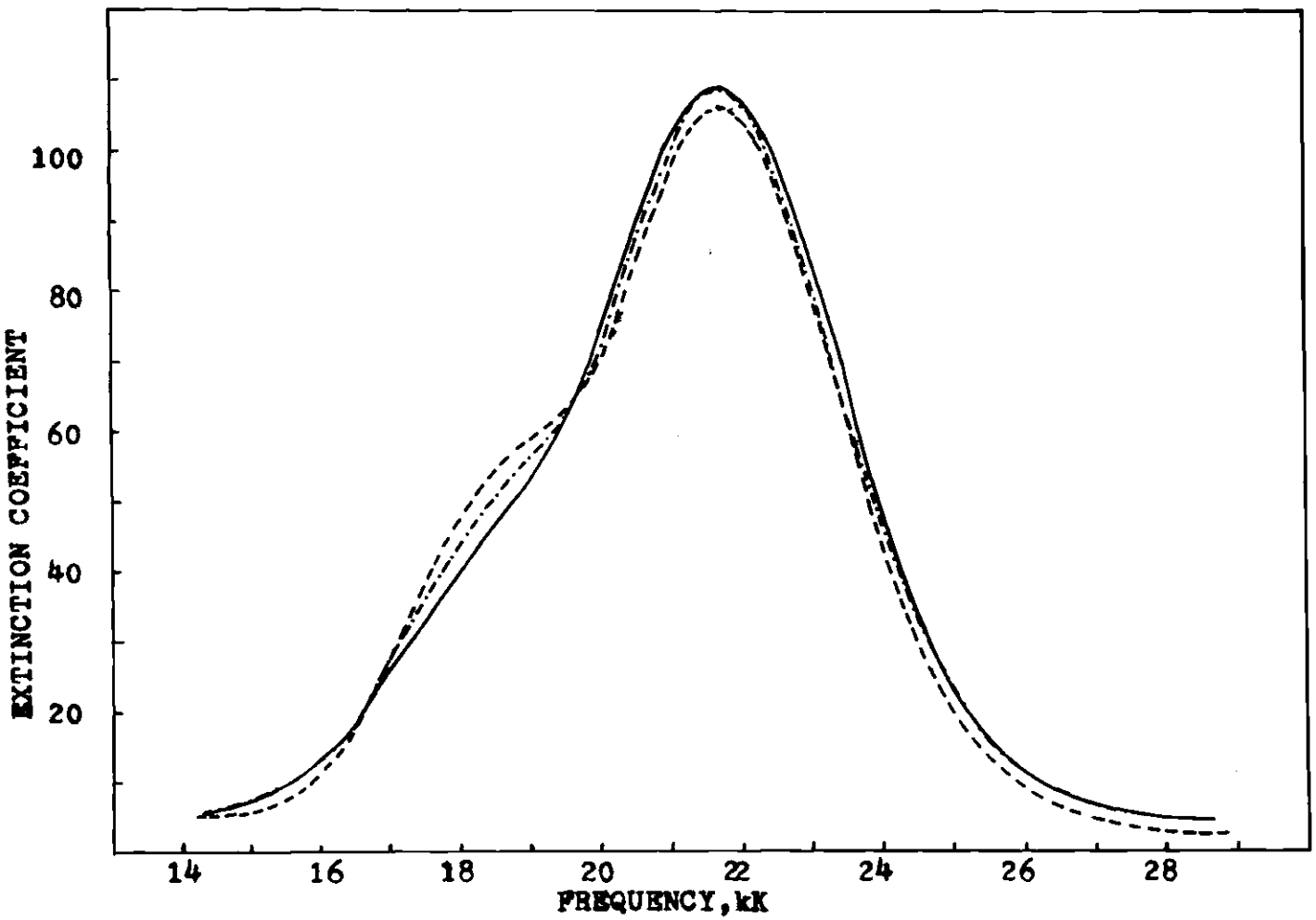

Figure 6. The Spectra of 1,5,9,13-Tetraaza-2,4,4,10,12, 12-hexamethylcyclohexadecanenickel(II) Perchlorate in Water. (-·-·- 11 °C; ----- 39°C; ____ 63°C)

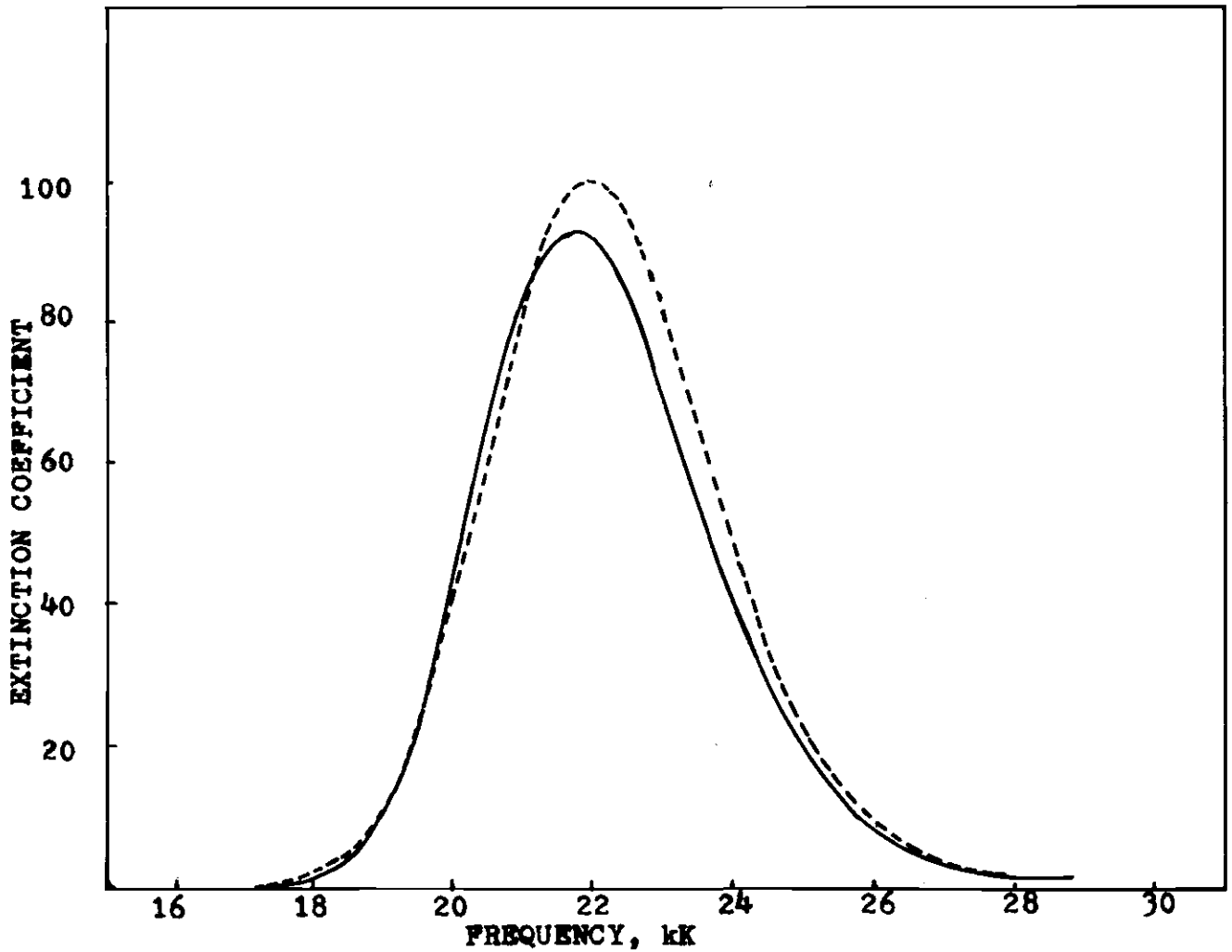

Figure 7. The Spectrum of cis (broken line) and trans (solid line) Hexamethyltetraazacyclotetradecanenickel(II) Complexes.

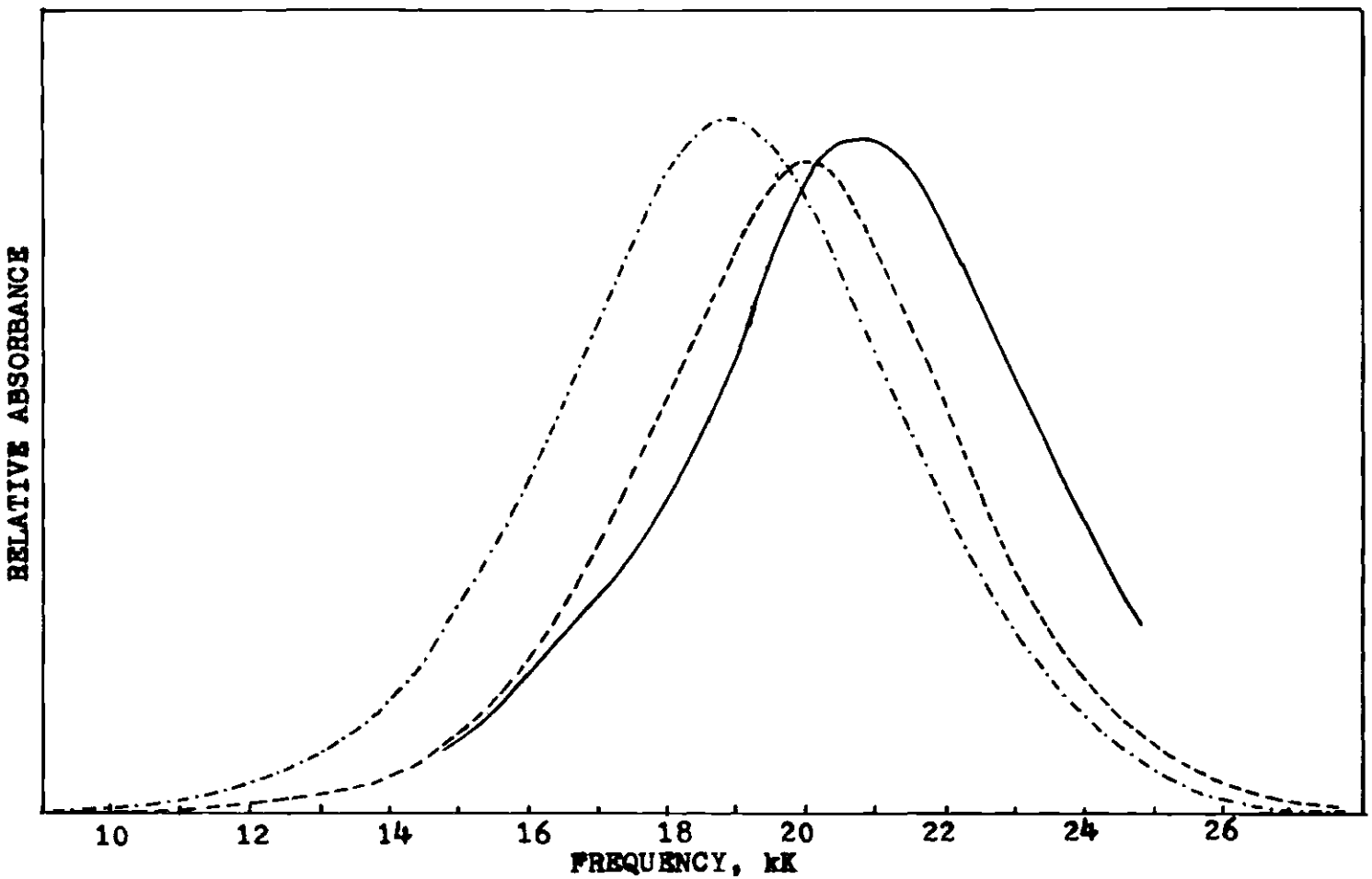

Figure 8. The Solution Spectra of bis(1,5 Diazacyclooctane)copper(II) Perchlorate. (-•-•-, pyridine; -----, water; ———, single crystal).

always have the lowest intensity of absorption when the light is polarized parallel to the longer direction of the face. Several crystals were chosen on the basis of largest area, optical properties of the surface and thinness. A selected crystal was mounted on a portion of a microscope slide by carefully placing PVC electrical tape on all edges of the crystal and securing it to the slide. The direction of the crystallographic axis relative to the edges of the slide was carefully noted. The mounted crystal was adjusted in the sample beam of the Beckman DK spectrophotometer so that the light passing through the sample impinged on the center of the shutter preceding the photodetector. A second portion of the microscope slide was taped with PVC tape so that a window of equivalent size to the sample was formed. The second slide was placed in the reference beam of the spectrophotometer. When polarized spectra were obtained, a sheet Polaroid type HN 38 was placed in both the sample and reference beam.

The crystals of the normal precipitation were found to be much too small to be used in the Beckman DK. This was indicated by either the automatic adjusting slit width opening to a maximum or lower than normal readings of the reference energy. Larger crystals of the bis(DACO) nickel(II) perchlorate were grown in 80% ethanol solutions by forming a saturated solution at 30^{o}C, and allowing crystals to form over a three week period in a water bath at 28^{o}C. Ethanolic solutions of bis-(DACO) copper(II) perchlorate were found to undergo some decomposition over such long periods of time. Large crystals of the copper complexes were grown by allowing very slow evaporation of the solvent of solutions placed between slides spaced with aluminum foil. Several of the resulting crystals were chosen using

the same criteria used in selection of the crystals from the first precipitations. The spectrum of a crystal of each of the nickel(II) and copper(II) compounds was determined. Each crystal had an area of about 0.3 mm^2 and a thickness of 0.05 to 0.10 mm.

The absorbance of each complex was obtained by subtracting a base line absorbance from observed absorption curve. The base line absorbance reflects differences in the amount of light passing through the sample relative to the reference beam because of differences in size of the windows formed by the PVC tape, scattering of light by the crystal, and differences in absorbance of the polarizers and slides. Examination of the absorbance of a slide taped in a similar manner as the one in the reference beam revealed that apparent absorbance was strongly dependent on the ratio of the size of the windows, but relatively independent of the frequency. This indicates that if scattering is not an important factor, the base line of our spectra will remain essentially constant in the frequency range that is considered. Although light scattering is known to increase with the frequency (19), scattering by the crystal is not expected to be great since we are dealing with a crystal of very uniform shape and surface. Accordingly then, we must select a base line representative of the absorbance readings due to the ratio of the size of the window in the sample to that of the reference beam. In the case of the bis(DACO) nickel(II) complex this was easily done since the range scanned covered portions where no electronic transitions occurred. In the case of the copper(II) complex, some extrapolation of the absorption curves was necessary to obtain the base line.

The curve of high absorbance which corresponds to the light being polarized

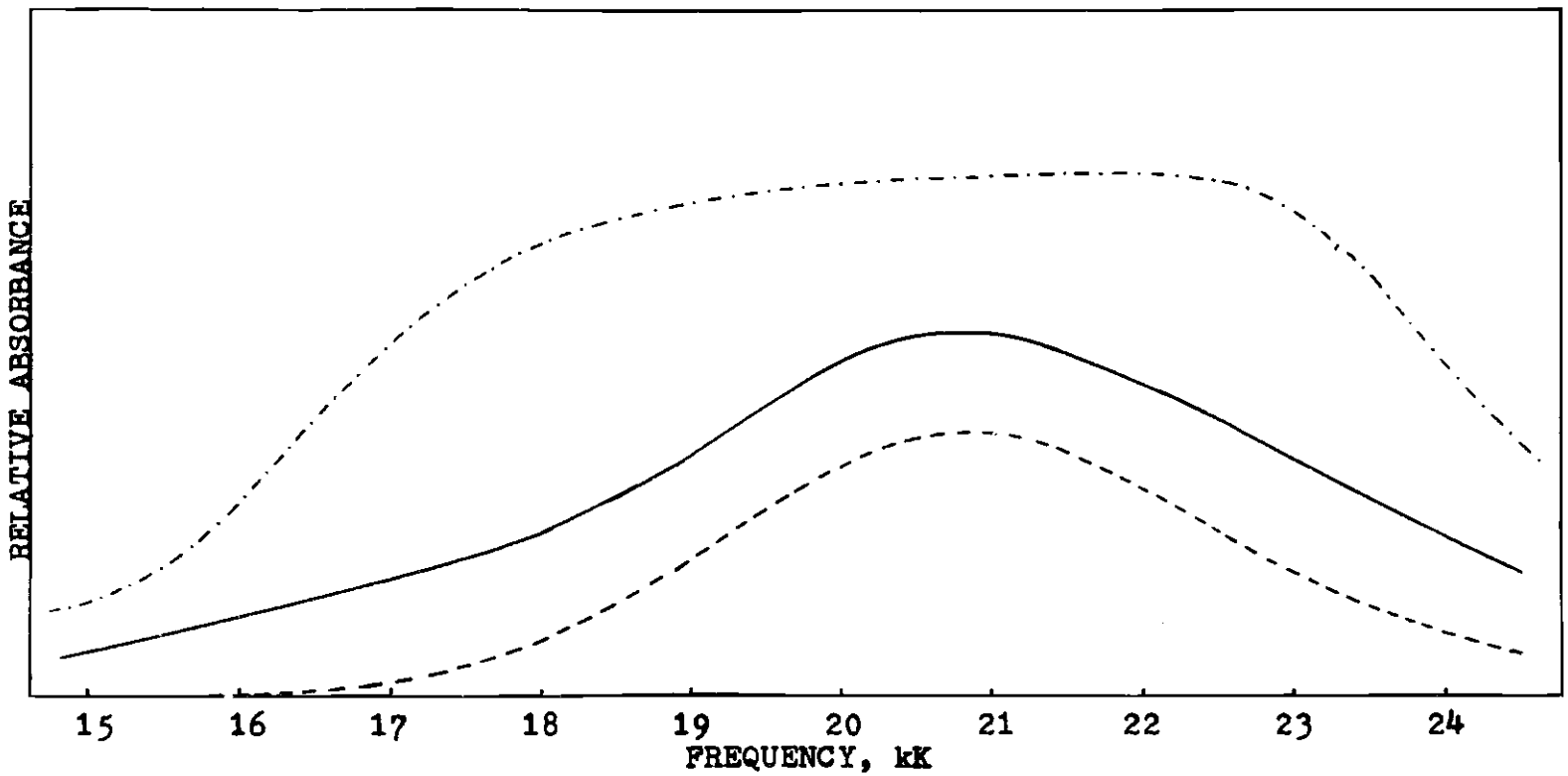

Figure 9. The Polarized Single Crystal Spectra of bis(1,5 Diazacyclooctane)copper(II) Perchlorate. (-.-.-, "direction one"; ———, unpolarized; -----, "direction two").

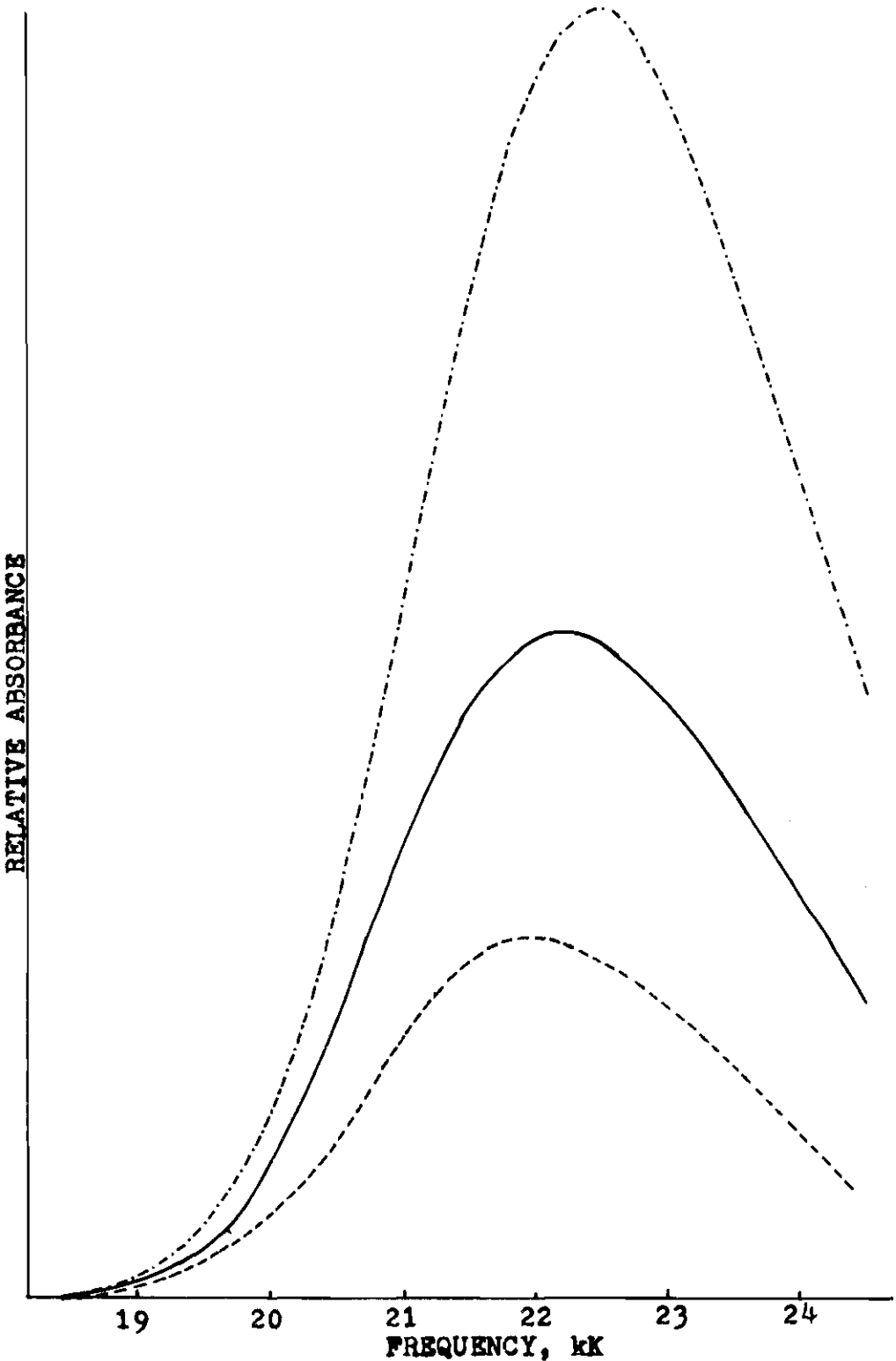

Figure 10. The Polarized Single Crystal Spectra of bis (1,5 Diazacyclooctane)nickel(II) Perchlorate Dihydrate. (The lines are defined as in Figure 9.)

parallel to the longer direction of the rectangular crystals will be known as "direction one" and a rotation of the polarizer 90^{o} to this direction will be known as "direction two." Due to the nature of the spectrophotometer and polarizers, the lowest energy obtainable corresponded to 16.6 kK and due to the absorbance of the polarizers the maximum energy obtainable corresponds to 24.6 kK. If the polarizers are removed, the range obtainable is from 16.6 to 28.5 kK.

Magnetic Susceptibility Determination

The majority of the magnetic susceptibilities determined at room temperature were measured using the Gouy method. A computer program written by Plymale (20) was used to calculate the results given in Table 1. The gram susceptibilities, χ_g, have been corrected for the susceptibilities of the sample tube and the displaced air. The molar susceptibility, χ_m, has been corrected for diamagnetism of the ligands, anions, and water present. The magnetic moments were calculated using the equation

$$\mu = 2.84 (\chi_m T)^{1/2}$$

where T is the absolute temperature. The deviation shown in Table 1 reflects the deviation of values obtained of measurements made at five field strengths.

The Faraday method was used to study the susceptibility as a function of temperature. In the Faraday method (21) the force developed by a small sample suspended in a magnetic field of constant H^{dH}/dz is measured. The field was developed using an Alpha Model 40-50A current regulated power supply coupled

Table 1. Magnetic Data Using the Gouy Method

Complex	$\chi_g \times 10^6$	$\chi_m \times 10^6$	μ
$Cu(DACO)_2(ClO_4)_2 2H_2O$	2.47± 0.07	1563± 37	1.91 ± 0.03
$Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$	-0.247± 0.015	122± 8	0.54± 0.02
$Ni(TAHD)(ClO_4)_2$	-0.293± 0.027	129± 15	0.56± 0.04
$Ni(TAH)(ClO_4)_2$	-0.360± 0.037	119± 21	0.53± 0.05
$Ni(HTTA)(ClO_4)_2$	-0.319± 0.079	129± 38	0.56± 0.08
$Ni(HTTB)(ClO_4)_2$	-0.386 ± 0.049	93± 26	0.47± 0.05

to an Alpha Model 9500 Electromagnet fitted with Heyding pole tips. Force on the sample was measured using a Cahn R. G. Automatic Electrobalance coupled to a Leeds and Northrup galvanometer. The torsion arm, the sample and suspension system were enclosed in a chamber so that all measurements of the force on the sample may be made in vacuum. The suspension system consisted of a thin copper wire fastened directly to the sample or in the case of powders, to the sample wrapped with a minimum of polyvinylchloride film.

The field of the magnet was determined using the equation

$$H \frac{dH}{dz} = \Delta m / \chi_a m$$

where Δm is the force of the field on the standard and the copper support, χ_a is the gram susceptibility of the standard and $\underline{m}$ is the mass of the standard. The

standard chosen was a platinum sample with a weight of 1.0853 g and $\chi_a = 0.971 \times 10^{-6}$ C.G.S. units. The position of maximum $H\frac{dH}{dz}$ was determined and used consistently in all measurements. The value of $H\frac{dH}{dz}$ was determined using six current settings.

The measurements of the samples were made in a similar manner. The force on the sample was measured at the six current settings used in the determination of the field. Temperatures other than room temperature were maintained by either dry ice-acetone or water baths in a Dewar vessel fitted between the pole faces.

The results of the calculations are given in Table 2. All values of χ_m have been corrected for the diamagnetism of the ligands, anions, water, and polyvinylchloride film using Pascal's constants (21). The constants were assumed not to vary over the temperature range considered.

Table 2. Magnetic Data Using the Faraday Method

	$Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$		
T	195°K	297°K	314°K
χ_m uncorrected	-148 ± 17	-141 ± 6	-141 ± 11
χ_m corrected	103 ± 17	110 ± 6	110 ± 11

In these calculations as well as the determination of the field strength, the effect of the copper support is considered negligible. An approximate calculation shows

that this assumption is justified. The copper support weighs 0.1 g and extends over a distance of 61 cm. Only a small portion of this support is in the region of maximum $H\frac{dH}{dz}$, but in our approximation we will assume that the entire mass is concentrated there. Ignoring the effect of the copper support, the field calculated at 9 amps is 5.427 C.G.S. units. Using this field and the value of $\chi_g = -8.58 \times 10^{-8}$ for copper, the force due to the copper support $\Delta m = -4.6 \times 10^{-8}$ g. The observed force on the platinum and support in this field is 5.724×10^{-6} g. Hence, ignoring the force of the support could influence the field only by 0.8%. The minimum force observed for any sample with the support at any temperature in this field is 1.15×10^{-6} g. Here the maximum error is 4.0%. Hence, the total maximum error is 4.8% and this is well within the experimental uncertainty of 10%. According to the above reasoning any error due to the susceptibility of support will produce results slightly lower than the true values.

CHAPTER III

THE RESOLUTION OF SPECTRAL DATA INTO COMPONENT TRANSITIONS

The Computer Program

The broad absorption bands of the electronic transitions of complexes approximate the shape of Gaussian error curves when plotted as a function of energy (3, 22). Often a region of the spectrum can be successfully represented as a linear combination of two or more such Gaussian curves. For many years the fitting of energy distribution curves has been done by laborious hand computations and plottings. Because of the trial and error nature of the fitting procedure, the time required to obtain a reasonably accurate fit is so great that the method will never be applied to the reduction of large amounts of data. An analog computer capable of speeding the trial and error method is commercially available, but this method is still tedious and not very accurate for complex spectra.

The general shape of a Gaussian error curve is shown in Figure 11. The equation defining such a curve is

$$E = \text{Phi}(1)\exp(-(X-\text{Phi}(2)/(\text{Phi}(3)^2))$$

where Phi(1) is the maximum peak height at Phi(2) and Phi(3) is the width near one-half Phi(1). An absorption curve having a single Gaussian component will have this form, where E is the absorbance and X is the frequency. An absorption curve

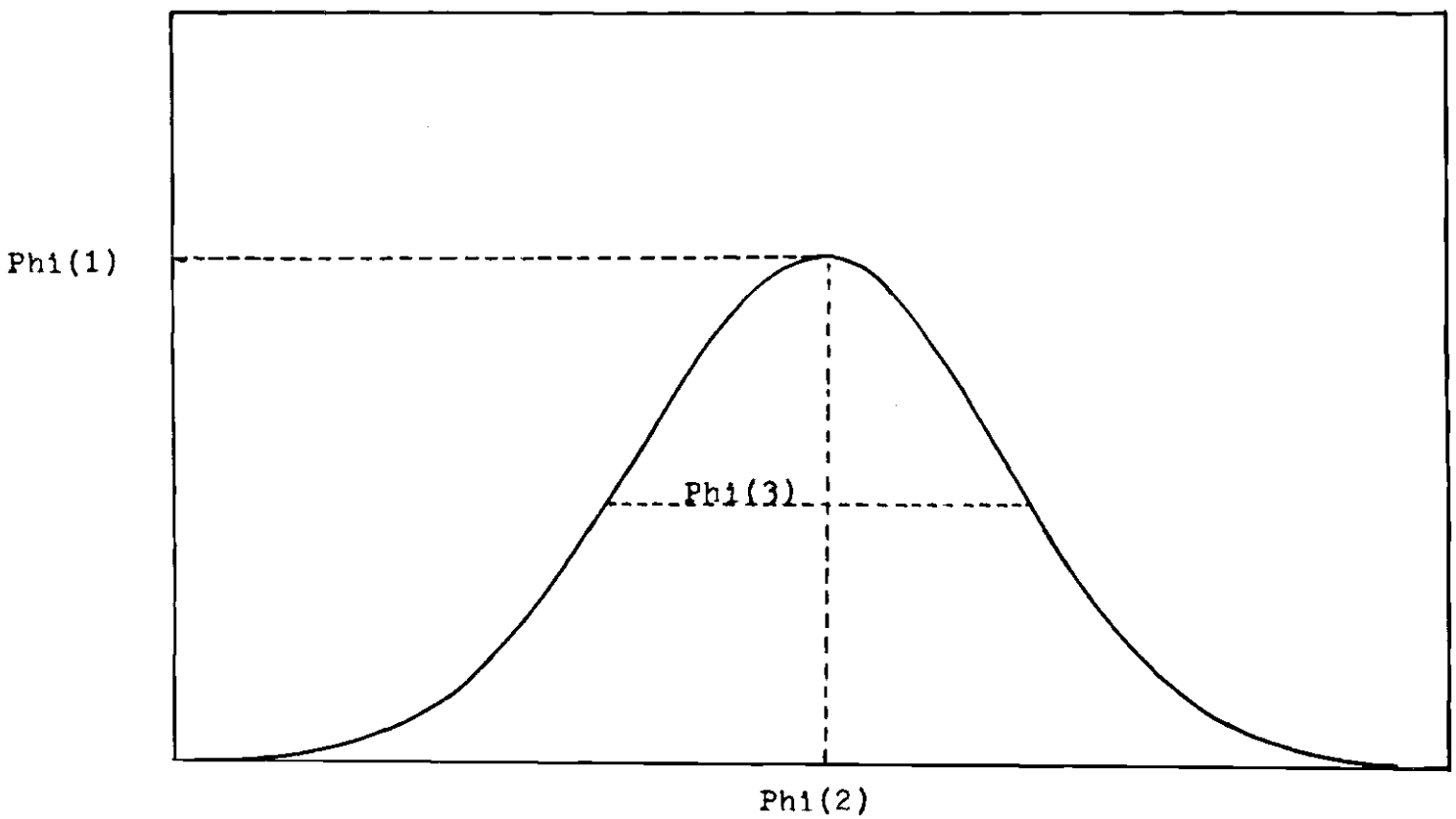

Figure 11. The Gaussian Error Curve.

having n Gaussian components will have the general form

$$Fx = E_1 + E_2 + ... + E_n$$

where Fx is the absorbance. Although spectral data are obtained as a continuous function of frequency, the computer program must deal with a finite number of fixed frequencies. For a specific frequency X(i) the appropriate equations are

$$Fx(i) = E_1(i) + E_2(i) + ...+E_n(i)$$

$$E_1(i) = Phi(1)exp-(Phi(2)-X(i))^2/(Phi(3))^2$$

$$E_2(i) = Phi(4)exp-(Phi(5)-X(i))^2/(Phi(6))^2$$

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$$E_n(i) = Phi(1+3(n-1))exp-(Phi(2+3(n-1))-X(i))^2/$$
$$(Phi(3+3(x-1)))^2$$

and

$$Fx(i) = E_1(i) + E_2(i) + ... + E_n(i).$$

The method used in resolving the experimental absorption curves into Gaussian components is a least-squares technique using a high speed digital computer. The function

$$S = \sum_{i=1}^{n} (Y(i) - Fx(i))^2$$

is to be minimized where n is the number of data points considered, Y(i) is the experimental absorbance at X(i). The function S from this point on will be known as the objective function.

Since the objective function is used as a basis for the comparison of the "goodness of fit," the influence of several factors should be noted. From the definition of the objective function one notes that its value is dependent on the number of data points. The computer is asked to make a comparison of fit to an experimental curve; hence n is a constant and the objective function is as good as any function which considers the influence of the number of data points. A more common means of estimating the "goodness of fit" is that of the standard error of estimate or the root mean square of the absorbance deviation about the fitted curve.

$$E = (S/n)^{1/2}$$

Consider a curve fitted with Gaussian components having a value of the standard error of estimate E. Suppose that the absorbance scale is decreased by a factor of F. Hence we have

$$E' = (S'/n)^{1/2}$$

If the scale is decreased by a factor F, then the deviation from any point must be decreased by F also. Hence

$$S' = \sum_{i=1}^{n} (F \times di)^2 = F^2 \sum_{i=1}^{n} (di)^2$$

where

$$di = Y(i) - Fx(i)$$

and

$$S = \sum_{i=1}^{n} (di)^2$$

Hence

$$E' = (F^2 \sum_{i=1}^{n} (di)^2/n)^{1/2}$$

$$E = (\sum_{i=1}^{n} (di)^2/n)^{1/2}$$

or $E' = FE$.

To make the standard error of estimate quantative, the curves should be normalized. But on what basis should they be normalized? If one chooses the maximum intensity of absorption as a basis for normalization then the comparison is not good between two curves one having its component bands at nearly the same energy and one having diffused components. Normalization on the basis of the area under the curve is probably the correct method, but then the normalized standard error of estimate becomes difficult to obtain, and once obtained, to relate to uncertainty in the experiment and the assumptions. In the resolved solution spectra, the extinction coefficients have values between 50 and 100 units. This means that if the components are diffused to the same extent, normalization on the basis of maximum intensity would change the standard error of estimates by as much as a factor or two. Since the curves with the lowest extinction coefficient correspond to those

with the most diffused components, normalization on the basis of area will not change the values greatly. Therefore, the standard error will not be complicated by normalization. The price that must be paid for this simplicity is that if the fit of different curves is compared on the basis of the standard error of estimate, no significance may be attached to any differences less than a factor of two or three. Single crystal spectra were normalized to the extent that the values obtained from the relative absorption scale were multiplied by one hundred so as to be of relatively the same scale as the molar extinction coefficients of the solution spectra.

As in all curve fitting procedures, the fitting process actually converges to a minimum. If the actual minimum is required an infinite number of iterations are required. In reality, only a relatively small number of iterations are required to be within the limits of the framework of the assumptions and experimental error. The search operation was terminated when the change of the parameters by 0.002 no longer produced an improvement. This value is well beyond the experimental accuracy of the instruments used.

Spectral data are usually experimentally obtained as a continuous function of either wave length or wave number. Since the computer program deals with a finite number of points, a choice of an interval between points must be made. The points must be close enough to define the features of the experimental curve and the Gaussian components. Experience has shown that data points at intervals of approximately 0.2 kK are sufficient. Since some curves are broader than others, between 33 and 61 points were used.

Resolution of Solution Spectra of Copper(II) Acetylacetonate

As a test of the computer method, the resolution of solution absorption spectra of the copper(II) acetylacetonate complex was reevaluated. Belford, Calvin and Belford (18) using crystal field arguments predicted that the visible spectrum should contain three transitions, $\underline{d}_{x^2-y^2} \rightarrow \underline{d}_{xz}, \underline{d}_{yz}$; $\underline{d}_{x^2-y^2} \rightarrow \underline{d}_{xy}$; and $\underline{d}_{x^2-y^2} \rightarrow \underline{d}_{xy}$. As the basicity of the ligands added to the axial positions increases, there should be a shift of all $\underline{d}$ to $\underline{d}$ transitions, except the $\underline{d}_{x^2-y^2} \rightarrow \underline{d}_{xy}$, to lower energy, the latter remaining unchanged. The absorption spectra of solution as resolved by the trial and error method substantiate their theory. The results of a typical computer resolution is shown in Figure 12. The standard error of estimation has a value of 0.598 units. The fit is so good that if the calculated summation of Gaussian components were plotted on a drawing of this scale, no deviation would be observed over the greatest part of the curve. The areas of poorest fit occur at the end ends of the absorption curve and the greatest deviation of any point is 1.3 extinction units. The results of the computer resolution and the resolution by Belford, Calvin, and Belford are shown in Table 3. We have used n-butanol instead of n-pentanol, but we will assume the two to be equivalent in base strength. The standard error of estimation are all of the same magnitude indicating that all the fits are all about equally good. No comparison of "goodness of fit" to Belford, Calvin and Belford's work may be made since they did not calculate a standard error of estimate. In Table 3 the Phi(n) have been designated as follows:

$$\text{Phi}(1) = A_1 = \text{absorbance of component one}$$

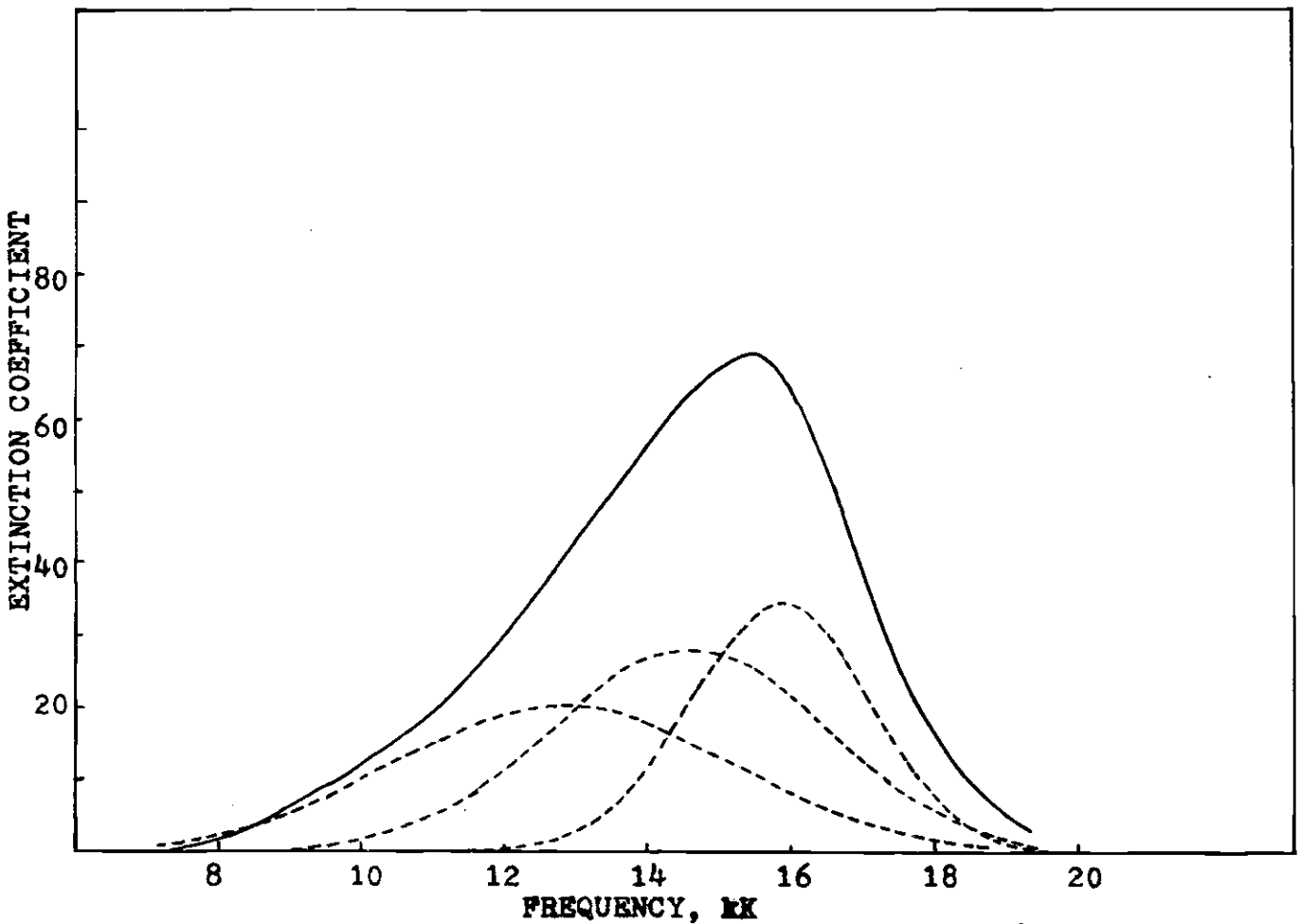

Figure 12. The Resolution of the Spectrum of Copper(II) Acetylacetonate (the solid line) in Pyridine into Component Bands (the broken lines).

Table 3. Gaussian Resolution of the Visible Spectra of Copper(II) Acetylacetonate

Belford, Calvin and Belford (15)

Solvent	A_1	K_1	W_1	A_2	K_2	W_2	A_3	K_3	W_3
Chloroform	26.3	18.81	3.82	34.1	15.19	3.38			
1,4-Dioxane	32.0	17.50	3.50	22.0	15.10	3.40	11.0	13.50	1.60
n-Pentanol	28.0	17.10	2.30	24.0	15.20	1.80	13.0	13.00	1.75
Pyridine	42.5	15.90	3.50	28.0	14.80	3.80	26.0	12.10	2.33

Computer Resolution

Solvent	A_1	K_1	W	A_2	K_2	W	A_3	K_3	W_3	E
Chloroform	25.54	18.29	2.80	25.32	14.98	1.76				0.62
Chloroform	25.31	18.59	2.37	19.91	15.67	1.59	14.73	14.39	1.61	0.52
1,4-Dioxane	24.39	17.27	2.19	20.35	15.44	2.73	11.91	14.11	1.65	0.34
n-Butanol	22.15	16.39	3.62	16.75	15.74	2.28	9.30	13.27	2.57	0.51
Pyridine	34.40	15.85	1.75	28.36	14.59	2.70	20.47	12.83	3.31	0.60

Phi(2) = K_1 = frequency in kK of the maximum of band one

Phi(3) = W_1 = the width of band one at one-half A_1

Phi(4) = A_2 = absorbance of component two

Phi(5) = K_2

Phi(6) = W_2

Phi(7) = A_3

Phi(8) = K_3

Phi(9) = W_3

The computer values of the E's were determined before the values of the above mentioned parameters were rounded off.

In accordance with Belford, Calvin, and Belford's theory, K_2 was assigned to the transition that does not change energy with the base strength. In the computer analysis K_2 using chloroform, 1,4-dioxane, and n-butanol and K_1 for pyridine must correspond to the transition that does not change energy. The transition K_1 for chloroform, 1,4-dioxane, and n-butanol, and K_2 for pyridine corresponds to another band. This order shown in Figure 12 requires that the $\underline{d}_{z}2$ orbital be the most stable in chloroform and that the $\underline{d}_{z}2$ orbital interact more strongly with pyridine than does the $\underline{d}_{x}2_{-y}2$ with the acetylacetonate anion. The latter requirement is not unreasonable since pyridine is known to produce very strong ligand fields (22). The order shown in Figure 12 differs from that suggested by Cotton (23) as a result of the analysis of the single crystal spectra of 2,2,6,6-tetramethylheptane-3,5-dione complex.

The computer resolution demonstrates that two bands decrease in frequency

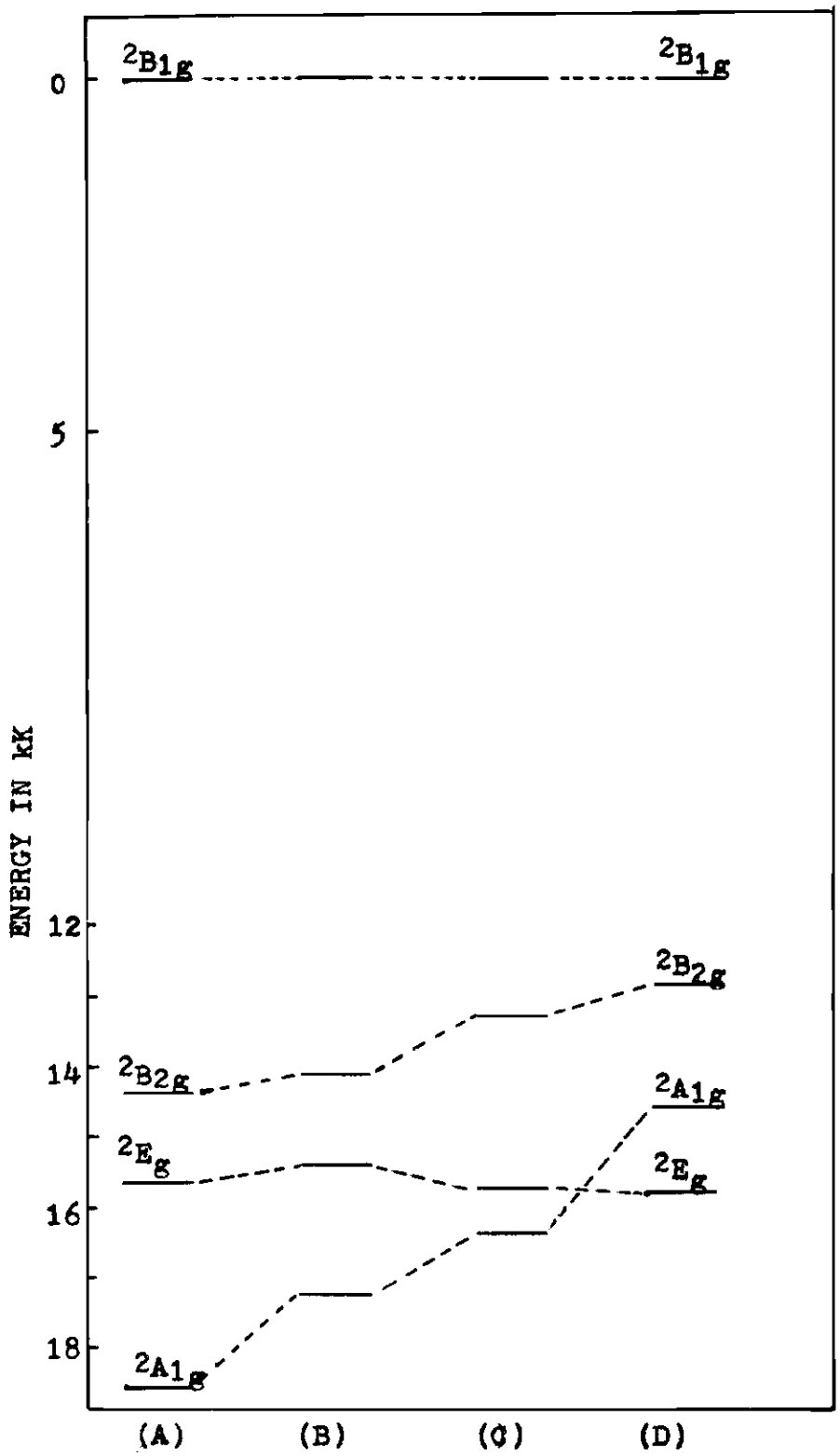

Figure 13. Energy States of Copper(II) Acetylacetonate as a Function of the Solvent. ((A), chloroform; (B), 1,4-dioxane; (C), n-butanol; (D), pyridine).

just as predicted even though the assignments of the bands differ somewhat from the previous assignment. This difference points out an additional advantage of computer resolution. All the possible widths, heights, and positions of the component bands are considered and the best fit is chosen without human bias. Hand resolution could be performed using an objective function just as the computer does, but one would spend an extremely large amount of time on one curve.

Resolution of Solution Spectra of $Ni(II)(DACO)_2$ and $Cu(II)(DACO)_2$ Ions

The solution spectra of the $Ni(II)(DACO)_2$ and $Cu(II)(DACO)_2$ ions show very little shift or change in shape as the solvent changed. This is probably due to the fact that the DACO ligands block the axial positions so well that the solvent does not greatly effect the d subshell of the metal ion. This high degree of blocking is good because it preserves the square-planar structure, but because of it we can not study the nature of the d to d transitions in the same manner as Belford, Calvin and Belford. But since we are attempting to evaluate the number as well as the nature of the d to d electron transitions, worthwhile information may be obtained by fitting the observed spectra to Gaussian components.

If the calculations by Maki (1) of square-planar nickel(II) complexes are at least qualitatively correct, the transitions, not necessarily in order, are as follows:

$$^1A_{1g} \rightarrow {}^1A_{2g}$$

$^1A_{1g} \rightarrow {}^1B_{2g}$

$^1A_{1g} \rightarrow {}^1E_g$

$^1A_{1g} \rightarrow {}^1B_{1g}$

Maki did not consider the possibility of any of these possible transitions being two-electron transitions. Two-electron transitions are of such low intensity that they are not usually observable and can be eliminated from our analysis. The symmetry of each level corresponds to the product of the symmetry of the appropriate one-electron functions (24). If the ligand field is assumed to be of D_{4h} symmetry, the two electron functions are composed as follows (see next chapter):

$^1A_{1g}$ $(d_{x^2-y^2})(d_{x^2-y^2})$

$^1B_{1g}$ $(d_{x^2-y^2})(d_{z^2})$

$^1B_{2g}$ $(d_{xy})(d_{z^2})$

^1E_g $(d_{x^2-y^2})(d_{xy}, d_{zy})$

$^1A_{2g}$ $(d_{x^2-y^2})(d_{xy})$

In the strong field limit the transition from $^1A_{1g} \rightarrow {}^1B_{2g}$ is a two electron

transition and need not be considered. If the possibility of symmetry lower than D_{4h} is included in our analysis, we must allow for the degenerate ^1E_g being split. Hence, the maximum number of observable transitions in a field of D_{4h} symmetry is three, and the maximum number in fields of lower symmetry is four. In our search, the possibility that there were one to four components in the observed visible absorption band was considered.

The results of the resolution of the visible spectra of the nickel complex are given in Table 4. The results indicate that improved fit is observed as the number of components is increased. This is to be expected since one can always describe any curve better when one has increased freedom due to additional parameters. But note what occurs when the search is conducted for four components. Three peaks of relatively the same absorption and width and one of very small and negative absorption are found. The three peaks of higher absorption agree fairly well with those found in the three peak resolution. This indicates that the maximum number of components is very probably three and that the use of D_{4h} symmetry is justified. We can not rule out a two component fit since the fit is as good as the three peak fit.

On the basis of the above analysis the ligand field of bis(DACO) may be assumed to be D_{4h}. From crystal field arguments the copper(II) complex may have no more than three d to d transition in the visible band; therefore the maximum number of components will be limited to three. The results of the resolution of the spectral data are given in Table 4 and indicate that either two or three components are necessary to describe the spectral data. The two sets of values

Table 4. The Resolution of the Spectral Data of Aqueous Solutions

Bis(DACO)copper(II) Perchlorate					
Number of Peaks		1	2	3	3
	A_1	89.40	49.88	32.75	33.49
Band one	K_1	19.93	19.79	18.96	17.88
	W_1	3.23	3.95	3.54	2.77
	A_2		42.47	32.30	49.10
Band two	K_2		20.09	20.13	19.97
	W_2		2.30	2.06	2.01
	A_3			31.63	36.70
Band three	K_3			20.74	21.67
	W_3			3.53	2.76
	E	2.01	0.16	0.14	0.22
Bis(DACO)nickel(II) Perchlorate					
Number of Peaks		1	2	3	4
	A_1	90.58	49.30	38.33	40.86
Band one	K_1	22.64	22.14	21.49	21.63
	W_1	2.23	1.59	1.38	1.44
	A_2		49.28	41.99	37.02
Band two	K_2		23.28	22.76	22.87
	W_2		2.61	1.39	1.45
	A_3			37.39	35.93
Band three	K_3			23.79	23.72
	W_3			2.55	2.70

Table 4 (continued). The Resolution of the Spectral Data of Aqueous Solutions

Number of Peaks		1	2	3	4
Band four	A_4				-0.51
	K_4				26.57
	W_4				0.49
	E	4.49	1.12	0.43	0.27

for the three peak search are the results of two independent searches. One set indicates that the computer obtained a local minimum rather than the overall minimum. To avoid the possibility of mistaking such local minima, the search procedure was conducted several times using different starting points. If the direction of search always converges to a particular point without regard to the direction of approach, we can be fairly sure of having the true minimum.

Resolution of Single Crystal Spectra

The electric dipole mechanism is the only mechanism of importance for the absorption of light by complex ions (21). In order for a transition between states of equivalent spin to occur, the integral $\int \Psi_{ground} U \Psi_{excited}$ must transform like the total symmetric representation. The electric dipole operator U transforms like the x, y and z axes and is of odd symmetry. Since the d wave functions are always of even symmetry, the integral $\int \Psi_{ground} U \Psi_{excited}$ is

not totally symmetric and transitions should not occur. In centrosymmetric complexes, the way that these integrals become symmetric is by mixing the excited or ground wave function with an appropriate vibrational wave function. In complexes of D_{4h} symmetry light polarized in the $\underline{x}$ or $\underline{y}$ direction is of E_u symmetry and light polarized in the $\underline{z}$ plane is of A_{1u} symmetry. Hence the proper vibrational wave functions are different in the different directions. The symmetries of the normal modes of vibration of a molecule of D_{4h} symmetry have been found to be (24) $2A_{1g}$, B_{1g}, B_{2g}, E_g, $2A_{2u}$, B_{2u} and $3E_u$. These states were found by assuming that each atom in the complex could move in any direction.

The transitions that will be considered for the nickel(II) complex of D_{4h} symmetry are $^1A_{1g} \rightarrow {}^1A_{2g}$, ^1E_g and $^1B_{1g}$ and for the copper(II) of D_{4h} symmetry, $^2B_{1g} \rightarrow {}^2B_{2g}$, ^2E_g and $^2A_{1g}$. The symmetry of the products of the ground state, excited state and the polarized light are as follows:

	$\int \Psi_g U_z \Psi_{ex}$	$\int \Psi_g U_{xy} \Psi_{ex}$
$A_{1g} \rightarrow A_{2g}$	A_{1u}	E_u
$A_{1g} \rightarrow B_{1g}$	B_{2u}	E_u
$A_{1g} \rightarrow E_g$	E_u	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$
$B_{1g} \rightarrow A_{1g}$	B_{2u}	E_u
$B_{1g} \rightarrow B_{2g}$	A_{1u}	E_u
$B_{1g} \rightarrow E_g$	E_u	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$

Since the product of any symmetry times itself will always produce a totally symmetric state, the transitions which have the symmetry of the normal modes of vibration become vibronically allowed. If we assume that all the vibronic interactions are equally effective the polarization of the transitions should be observed as given in Table 5.

Table 5. Polarization with Vibronic Coupling

	z	x, y
$A_{1g} \rightarrow A_{2g}$	Forbidden	Allowed (E_u)
$A_{1g} \rightarrow B_{1g}$	Allowed (B_{2u})	Allowed (E_u)
$A_{1g} \rightarrow E_g$	Allowed (E_u)	Allowed (A_{2u}, B_{2u})
$B_{1g} \rightarrow B_{2g}$	Forbidden	Allowed (E_u)
$B_{1g} \rightarrow E_g$	Allowed (E_u)	Allowed (A_{2u}, B_{2u})
$B_{1g} \rightarrow A_{1g}$	Allowed (B_{2u})	Allowed (E_u)

The polarized spectra of the DACO complexes of nickel(II) and copper(II) shown in Figures 9 and 10 were determined without knowing the position of orientation of the complex within the crystal. Through the use of the "selection rules" the orientation of the complex ion in the crystal and the nature of the component

transitions can be deduced.

The polarized spectrum of the copper(II) complex in "direction one" is not Gaussian in shape. If this spectra is compared with the one polarized in "direction two" we observe that only the center portion of "direction one" remains in "direction two." This indicates that there must be component bands at both ends of the spectra. The computer resolution is given in Table 6. Each set of values was determined independently. Note that in both polarizations and unpolarized spectra we obtain a center component at 20.7 kK and the relative absorbance of 32 units. This component must be an unpolarized band. The other two components undergo a considerable change with the direction of polarization. The band position changes very little with the only exception being the band of very low absorbance at 19.75 kK in "direction two." The position of a band of such low absorbance has no significance since it may only be a peak obtained to account for experimental deviation or deviation of other bands from the calculated Gaussian shape. The fact that the absorbance of the bands in the two directions average very nearly the value of the unpolarized is significant. An equal amount of light in "direction one" and "direction two" strikes the sample when unpolarized light is used. Since no distinction is made between the two directions of polarization, the observed adsorption of light by the sample should be the average value of that absorbed in "direction one" and "direction two."

If we assume D_{4h} symmetry, the transitions for the copper(II) complexes are all vibronically allowed in the $\underline{xy}$ direction and only the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition is forbidden in the $\underline{z}$ direction. Our resolution indicates that we have one transition

Table 6. Resolution of Single Crystal Data

	A_1	K_1	W_1	A_2	K_2	W_2	A_3	K_3	W_3	E
Bis(DACO)copper(II) Perchlorate Dihydrate										
Unpolarized	16.92	18.23	2.96	32.81	20.96	1.98	21.40	23.13	2.36	0.28
Direction One	54.95	18.16	2.56	32.82	20.78	2.07	52.03	23.04	2.13	0.81
Direction Two	2.91	19.75	2.04	32.35	20.83	2.14	5.78	23.49	1.85	0.19
Bis(DACO)nickel(II) Perchlorate Dihydrate										
Unpolarized	20.90	21.35	1.31	29.00	22.30	1.57	21.20	23.78	1.56	0.17
	23.80	21.44	1.30	39.00	22.98	1.94				0.20
Direction One	18.50	21.60	1.50	61.10	22.19	1.58	43.70	23.80	1.76	0.28
	23.77	21.62	1.18	85.04	22.83	1.99				0.28
Direction Two	23.70	21.69	1.49	0.01	22.47	1.59	12.00	23.41	1.44	0.19
	24.80	21.74	1.52	11.00	23.50	1.37				0.19

that undergoes a 19 fold change with direction, and one that undergoes a nine fold change with direction. The question that must be answered is whether one or both of the transitions that undergo this change represent a polarization due to a lack of the proper vibrational state or whether only a difference in effectiveness of the vibronic coupling occurs. Perhaps this question may be answered by examining the vibronic coupling of other systems. Liehr (25) has calculated that the most effective means of promoting intensity in transitions in octahedral symmetry is through coupling with the T_{1u} vibronic state. The T_{1u} state corresponds to a vibration which is equivalent to the metal ion vibrating in an octahedral cage of ligands. We may consider the bis DACO complexes as altered octahedra and assume that the effective vibrations of an octahedral complex are also the effective ones for square-planar complexes. This means that in a field of D_{4h} symmetry the most effective vibronic coupling will occur using the A_{2u} and E_u vibronic states.

Ferguson (5, 6) in his studies of the polarized spectra of the essentially planar bis-salicylaldiminato copper(II) and nickel(II) complexes of D_{2h} or lower symmetry observed that polarization occurred when none was predicted by vibronic coupling. However, he was able to explain the spectra of these complexes and the methyl derivatives in a consistent manner using the above reasoning. Piper and Belford (26) countered with an alternate method. They took the approach that some coupling must be more effective than others but these are to be determined by each molecule's particular symmetry.

Let us approach the problem using the method of Piper and Belford (26).

We will assume that the ligand field may be described by D_{4h} symmetry. Since we have assumed D_{4h} symmetry the only way polarization will occur is if one direction of polarization is in the $\underline{z}$ direction and the other direction is perpendicular to the $\underline{z}$ direction. This is required because under D_{4h} symmetry $\underline{x}$ and $\underline{y}$ axis are indistinguishable. Examination of Table 5 reveals that the spectra may be explained only if the E_u and A_{2u} are the effective coupling vibrations. These states are the same states that are predicted to be the most effective by analogy to octahedral complexes.

If then the A_{2u} and E_u vibration states are the only ones effective in coupling, the center band at 20.8 kK may be assigned to the $^2B_{1g} \rightarrow {}^2E_g$ transition. Since the crystal field arguments indicate that the $^2B_{1g} \rightarrow {}^2B_{2g}$ should be of lower energy than the $^2B_{1g} \rightarrow {}^2E_g$, we conclude that the transitions of the copper(II) ion may be assigned to the experimentally resolved spectra as follows:

$$^2B_{1g} \rightarrow {}^2B_{2g} \quad 18.2 \text{ kK}$$

$$^2B_{1g} \rightarrow {}^2E_g \quad 20.8 \text{ kK}$$

$$^2B_{1g} \rightarrow {}^2A_{1g} \quad 23.8 \text{ kK}$$

It is encouraging to note that the component band undergoing the 19 fold change with direction is the band that is predicted to be forbidden in one of the directions; and that the band undergoing a nine fold change is the transition predicted to be vibronically allowed, but not very effectively so in one direction.

The single crystal spectra of the bis(DACO) nickel(II) perchlorate complex is shown in Figure 10. If only the intensity were changing with the direction of polarization without change of shape or position, the broad visible band could be rationalized as a single d to d transition with more effective coupling to certain vibrational modes. Infrared studies of square-planar complexes (27) indicate that transitions between vibrational states usually occur between 0.100 and 0.400 kK. Since the electronic transitions are coupled to different vibrational states when light is polarized in different directions, a shift up to 0.30 kK may be expected. Hence the observed shift, which is considerably greater than this, could probably best be explained by the presence of two or more component bands some of them being polarized.

Gaussian resolution limited to two and three components is given in Table 6. Resolution into two components gives a good fit in all three cases, but the position of the Gaussian components vary considerably. If a component is present and has appreciable intensity it should not change energy by amounts larger than the energy of the coupling vibration states. The two resolved component bands change from 21.4 to 21.7 kK and from 22.8 to 23.5 kK. Since this is a greater shift than we could normally justify and we can probably discount the two peak resolutions. The three peak resolution is somewhat better in that the maximum shift is 0.4 kK. Since no values of the experimental curve are known in the region above 24.5 kK the computer was given complete freedom to assign any curve it desired in this region. The results indicate that the greatest shift of energy of any resolved computer was given complete freedom to assign any curve it desired in this region.

The results indicate that the greatest shift of energy of any resolved component occurs with the component with its maximum nearest this range. Since the experimental curve is not known, we should treat the results of the resolution in this area with less faith than other areas.

The results of the resolution indicate that the component at 21.6 kK is allowed in both directions, the band at 22.3 kK is allowed in "direction one" and forbidden in "direction two," and the band at 23.7 kK changes intensity in the two directions. Using the three possible transitions and again assuming that the most effective coupling with vibronic states are the E_u and A_{2u} vibration we conclude that the component at 21.6 kK must be the $^1A_{1g} \rightarrow {}^1E_g$ transition and the other two components are the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions. If we require the same conditions to exist in the nickel(II) complex that existed in the copper(II) complex we must require that the B_{2u} mechanism remain relatively ineffective. Then the band at 23.7 kK may be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition on the basis that it undergoes a relatively large change in intensity with direction of polarization. This leaves only the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition to be assigned to the band at 22.3 kK on the basis that it is completely polarized in the xy direction.

If we assume D_{4h} symmetry, the high degree of polarization indicates "direction two" must be perpendicular to the xy plane or we would see some absorbance of the xy allowed transitions. Because of the fact that some of our resolved bands decrease to essentially zero absorbance in "direction two" we must conclude that the complex ions are very uniformly aligned within the crystal and that our polarization is aligned very well with the z axis and the xy plane of

the ions.

The question arises as to whether we are justified in assuming D_{4h} symmetry for our ligand field and our vibrational states. The resolution of solution spectra showed no evidence of any splitting of the ^2E_g state indicative of a ligand field of symmetry lower than D_{4h}; hence we are probably justified in assuming that the ligand field is D_{4h} symmetry. If the vibrational states are based on D_{2h} symmetry rather than D_{4h} symmetry, the only difference in the vibrational states is that the E_u state is split. As shown in Ferguson's study (5) lowering symmetry to D_{2h} will not change the selection rules for polarization perpendicular to the xy plane and polarization parallel to the xy plane will depend on the direction of polarization within the plane. The difference in the xy plane will only influence the degenerate components of the E_g state, but will not forbid both of the degenerate components at any orientation within the plane. In other words, regardless of the direction we chose within the plane, the transitions to the E_g states will always be allowed and we may choose to use D_{2h} or D_{4h} vibrational symmetry without influencing the interpretation.

In the study of bis-n-methylsalicylaldiminatocopper(II) Ferguson (6) observed two bands that have no out-of-plane components and that there is some evidence of two additional bands which showed polarization in the xy plane, but these were uncertain because of the overlapping ligand absorption. These observations for a complex best described by D_{2h} symmetry may be related to our work if we take the liberty of assuming that it has D_{4h} symmetry. The first two bands may be assigned to the $^2B_{1g}$ to the $^2A_{1g}$ and $^2B_{2g}$ transitions not necessarily in

that order. The higher energy band or bands which are observed in the z direction as well as certain directions in xy plane may be assigned to the transitions from the $^2B_{1g}$ ground state to states stemming from the ^1E_g state. If we do not require that the A_{2u} and E_u states are the only effective states for vibronic coupling, then we are faced with the same problem that confronted us with the DACO complexes.

The polarized crystal spectrum of pentaamminecupric ammonium perchlorate (28) indicates the presence of a component at 17.0 kK which is unpolarized, a component at 15.5 kK which is polarized in the xy plane and a component at 13.5 kK which is observable in both directions. There is a possibility that the band at 13.5 kK undergoes a change in intensity, but it is doubtful whether the change is more than two fold. This band is assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition and is allowed by the B_{2u} vibronic wave function in the z direction. We must conclude that the B_{2u} coupling must be more effective in this case. Similar observations are made in the studies of the platinum chlorides (29).

Comparison of the above studies reveals that perhaps the best approach to interpretation of the polarization of single crystal spectra is that not all predicted vibronic couplings are equally effective. The effectiveness of each is dependent upon the ligand system. Since we are making comparisons of systems of the type ML_4 where L is a one atom ligand in some cases and in other cases it is part of a much larger chelate system, differences are not surprising. Surely there must be some restrictions of the vibronic states of complicated systems.

CHAPTER IV

ENERGY LEVEL CALCULATIONS OF SQUARE-PLANAR NICKEL(DACO)$_2$(ClO_4)$_2$

The use of ligand field theory has had considerable success in explaining the physical properties of the transition metal ions. The nature of the d subshell determines the physical properties of transitional metal complex ions, and this is where ligand field theory concentrates its attention. The theory has the advantage over molecular orbital theory in that the calculation is reduced to an atomic calculation. However, highly covalent bonding complexes such as $Ni(CO)_4$ and $Fe(CN)_6^{4-}$ are not well described by ligand field theory. This is true because we are no longer dealing with atomic orbitals.

Ligand field theory finds its origin in crystal field theory. Crystal field theory assumes that the effects of the ligands on the energy levels of the central metal ion can be explained by considering the ligands to be point charges or point dipoles. The electrostatic interaction between the point charges or dipoles and electrons causes a splitting of the originally degenerate d orbitals of the metal ion. The splitting is dependent on the symmetry arrangements of the ligand and the intensity of the interaction. The intensity of interaction can be calculated if the atomic orbitals, a parameter R which relates to the distance between the ligand and the central metal ion, the effective point charge and the point dipole are known. Rather than estimating the above mentioned parameters, the

interactions are often described in terms of orbital splitting parameters.

Ligand field theory differs from crystal field theory by not assuming that the interaction is a purely electrostatic interaction. Ligand field theory admits that there is some covalent bonding but not so much that the approach of crystal theory is undermined. A comparison of the relative amounts of covalency can be obtained by examining the nephelauxetic series of ligands. Jorgensen (22) has given the series in terms of increasing degree of covalency as

$$F^- < H_2O < \text{urea} < NH_3 < en \sim Ox^{2-} < \underline{N}CS \ll Cl \sim CN^- < Br^- < I^-$$

The ligand DACO should occupy a position in the series in the neighborhood of en. This indicates that ligand DACO provides for a relatively small amount of covalency and the $Ni(DACO)_2$ complex ion should be in the framework of ligand field theory.

Our calculation will differ from Maki's (1) calculation for square-planar nickel(II) complexes in several aspects. Maki's calculation is a crystal field calculation while ours is a ligand field calculation. Maki had to use atomic wave functions with radial functions and her choice was Slater atomic orbitals. We will use atomic orbitals of the general form

$$\underline{d}\ m_1 = R(r)\ Y_2^{ml}$$

where R(r) is the radial part and Y_2^{ml} is the spherical harmonic. In our calculation the radial part is never evaluated or approximated. Furthermore, the parameter R, the effective point charge and the point dipole is not evaluated or assigned

specific values. Instead, the energy levels are calculated using the one electron integrals evaluated from $Cu(II)(DACO)_2(ClO_4)_2$ spectra. The ligand field is assumed to be of D_{4h} symmetry. Also, the usual assumption is made that the spin function may be regarded as being entirely independent of the orbital function and, to the first approximation, to have no influence on the energy of the levels. The total electronic state of the nickel(II) and copper(II) ion will be described in terms of functions of $\underline{d}^2$ and $\underline{d}^1$ holes, respectively.

The $\underline{d}$ orbitals form a basis for a representation of the group D_{4h} which contain the irreducible representation a_{1g}, b_{1g}, b_{2g}, and e_g using the method outlined by Ballhausen (24). The five linear combinations of the $\underline{d}$ orbitals forming the irreducible representations are found by quantization about the fourfold axis. Using the phase convention of Condon and Shortley (30) and dropping the common factors of R(r) and $(5/4)^{1/2}\pi$ the spherical harmonics are

$$\underline{d}\,\pm 2 = Y_2^{\pm 2} = \sqrt{3/8}\,(x \pm iy)^2$$

$$\underline{d}_1 = Y_2^1 = \sqrt{3/2}(x + i\,y)z$$

$$\underline{d}_0 = Y_2^0 = 1/2\,(3z^2 - r^2)$$

$$\underline{d}_{-1} = Y_2^{-1} = \sqrt{3/2}\,(x - iy)z$$

where the subscripts of the $\underline{d}$ orbitals reflect the value of m_1. Since the system has been quantized along the fourfold axis, the wave functions must be diagonal with respect to this axis. In Table 7 the $\underline{d}_1$, $\underline{d}_0$, and $\underline{d}_{-1}$ are seen to be "pure" orbitals, whereas the $\underline{d}_2$ and $\underline{d}_{-2}$ can mix under a C_2' rotation. Then

$$\Psi_{\pm} = a\underline{d}_2 \pm b\underline{d}_{-2}.$$

Table 7. Transformation Properties of d Orbitals

in D_{4h} Symmetry

	E	C_2 $z \to z$, $x \to -x$, $y \to -y$	C_4 $z \to z$, $x \to y$, $y \to -x$	C_2' $z \to -z$, $x \to y$, $y \to x$
d_2	d_2	d_2	$-d_2$	$-d_{-2}$
d_1	d_1	$-d_1$	$-id_1$	id_{-1}
d_0	d_0	d_0	d_0	d_0
d_{-1}	d_{-1}	$-d_{-1}$	id_{-1}	$-id_1$
d_{-2}	d_{-2}	d_{-2}	$-d_{-2}$	$-d_2$

By application of the C′ operation and normalization the orbitals are

$$\Psi_{\pm} = \frac{1}{\sqrt{2}} (\underline{d}_2 \pm \underline{d}_{-2}).$$

Since the trace under C_4 of a_{1g}, b_{1g}, b_{2g} and e_g is real, $\underline{d}_1$ and $\underline{d}_{-1}$ must be grouped together. Hence, the real positive angular portion of the wave functions are obtained from the Condon and Shortley spherical harmonics and are found to be

$$\underline{d}_{x^2-y^2} = 1/\sqrt{2}\,(\underline{d}_2 + \underline{d}_{-2}) = \sqrt{3}/2\,(x^2-y^2)$$

$$\underline{d}_{z^2} = \underline{d}_0 = 1/2\,(3z^2 - r^2)$$

$$\underline{d}_{xy} = \frac{1}{\sqrt{2}}\,(\underline{d}_2 - \underline{d}_{-2}) = \sqrt{3}\,(xy)$$

$$\underline{d}_{xz} = -\frac{1}{i\sqrt{2}}\,(\underline{d}_1 - \underline{d}_{-1}) = \sqrt{3}\,(xz)$$

$$\underline{d}_{yz} = -\frac{1}{i\sqrt{2}}\,(\underline{d}_1 + \underline{d}_{-1}) = \sqrt{3}(yz)$$

Character tables (3) for D_{4h} symmetry reveal that the orbitals have the following symmetry:

b_{1g}: $\underline{d}_{x^2-y^2}$

a_{1g}: $\underline{d}_{z^2}$

b_{2g}: $\underline{d}_{xy}$

e_g: $\underline{d}_{xz}$, $\underline{d}_{yz}$

The energy of the one positron states may be written as

$$E_{(b_{1g})} = \epsilon_0 + \int \phi^*(b_{1g})\, V_{D_{4h}}\, \phi\,(b_{1g})dy = \epsilon_0 + \Delta_1$$

$$E(b_{2g}) = \epsilon_0 + \int \phi^*(b_{2g})\, V_{D_{4h}}\, \phi\,(b_{2g})dy = \epsilon_0 + \Delta_2$$

$$E_{(e_g)} = \epsilon_0 + \int \phi^*(e_g)\, V_{D_{4h}}\, \phi(e_g)\, dy = \epsilon_0 + \Delta_3$$

$$E_{(a_{1g})} = \epsilon_0 + \int \phi^*(a_{1g})\, V_{D_{4h}}\, \phi(a_{1g})\, dy = \epsilon_0 + \Delta_4$$

where E(n) is the energy of the nth state, ϵ_0 is the energy of the free ion state, ϕ_n is the nth orbital, and Δ_n is the stabilization of the nth state. From the definition of the energies of the levels, the energy of the one-electron transitions are

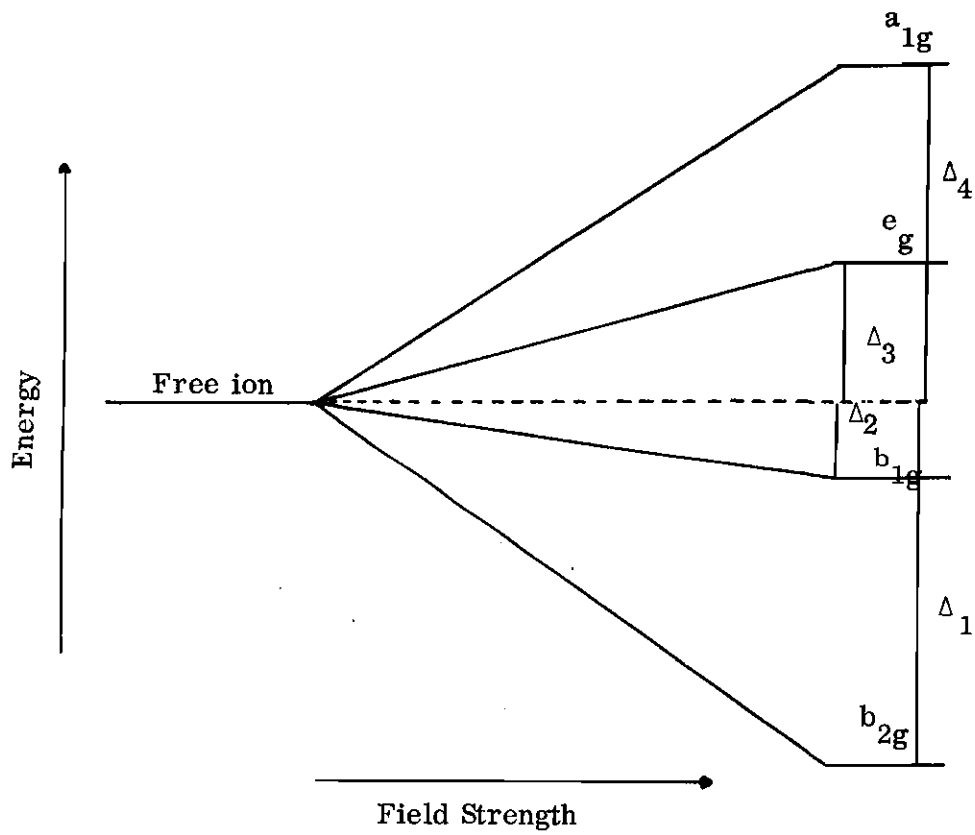

Figure 14. Qualitative Splitting of the d Subshell in D_{4h} Symmetry.

the following:

$$E_{(b_{1g})} - E_{(b_{2g})} = \Delta_2 - \Delta_1 = W_1'$$

$$E_{(e_g)} - E_{(b_{2g})} = \Delta_3 - \Delta_1 = W_2'$$

$$E_{(a_{1g})} - E_{(b_{2g})} = \Delta_4 - \Delta_1 = W_3'$$

Using the "center-of-gravity" rule, the splitting from the center-of-gravity may be calculated.

$$\Delta_1 + \Delta_2 + 2\,\Delta_3 + \Delta_4 = 0$$

$$\Delta_2 = W_1 + \Delta_1$$

$$\Delta_3 = W_2 + \Delta_1$$

$$\Delta_4 = W_3 + \Delta_1$$

Using the definition of the energy levels, the one-electron integrals may be evaluated in terms of the Δ's.

$$\Delta_4 = \langle \underline{d}_0 \mid V \mid \underline{d}_0 \rangle$$

$$\Delta_3 = \langle \underline{d}_1 \mid V \mid \underline{d}_1 \rangle$$

$$\Delta_2 = \langle 1/\sqrt{2}\,(\underline{d}_2 - \underline{d}_{-2}) \mid V \mid 1/\sqrt{2}\,(\underline{d}_2 - \underline{d}_{-2}) \rangle =$$

$$< \underline{d}_2 \mid V \mid \underline{d}_2 > - < \underline{d}_2 \mid V \mid \underline{d}_{-2} >$$

$$\Delta_1 = < 1/\sqrt{2}\,(\underline{d}_2 + \underline{d}_{-2}) \mid V \mid 1/\sqrt{2}\,(\underline{d}_2 + \underline{d}_{-2}) > =$$

$$< \underline{d}_2 \mid V \mid \underline{d}_2 > + < \underline{d}_2 \mid V \mid \underline{d}_{-2} >$$

$$2 < \underline{d}_2 \mid V \mid \underline{d}_2 > = \Delta_1 + \Delta_2$$

$$< \underline{d}_2 \mid V \mid \underline{d}_2 > = \frac{\Delta_1 + \Delta_2}{2}$$

$$< \underline{d}_2 \mid V \mid \underline{d}_{-2} > = \Delta_1 - \frac{\Delta_1 + \Delta_2}{2} = (\Delta_1 - \Delta_2)/2$$

If the values of the W 's were known, the energy levels of the square-planar nickel(II) complexes could be calculated.

The three visible transitions of copper(II) $(DACO)_2$ complex ion correspond to the transitions in a single positron case. Furthermore in Chapter III these transitions have been shown to correspond to W_1', W_2', and W_3' in that order. Rather than treat the W's as variable parameters for the calculation, a relationship between the W's of the two ions is assumed. The atomic orbitals for the nickel(II) ion are expected to be somewhat smaller due to imperfect shielding of one electron by another in the same subshell. The nuclear charge and the number of $\underline{d}$ electrons increases by one when going from nickel (II) to copper (II). Since shielding is imperfect due to the shape of the orbitals, an increase of the nuclear charge by one unit causes a reduction in size of the entire $\underline{d}$ subshell.

Since the ligand field interaction is mainly an electrostatic interaction, the larger d subshell is expected to interact to the greater extent. The above reasoning assumes that the distance between the central metal nucleus and the ligand nucleus is constant in the two complexes. If x-ray structural determinations of other four coordinate systems are considered, the conclusion is reached that perhaps small differences are probable. The bis-n-methylsalicylaldiminato) (31, 32) nickel(II) and copper(II) complexes are reported to have intramolecular distances and angles essentially the same, but the copper(II) complex is completely square-planar and the metal to ligand distances are 0.1 Å longer. On the other hand the bis-salicylaldiminato (33,34) nickel(II) complex is completely square-planar, but again the metal-ligand distance is 0.1 Å longer for the copper(II) complex. On the basis of the above complexes, one can not make general statements that metal to ligand distance will be 0.1 Å shorter in the $[\,Ni(II)(DACO)_2]$ complex. However, we feel safe in assuming that the metal to ligand distances do not vary greatly. To account for the possibility of stronger ligand fields due to difference in the size of ions and in metal to ligand distance, a factor P will be included in the calculation. The factor P is defined such that

$$W_1 = PW_1'$$

$$W_2 = PW_2'$$

$$W_3 = PW_3' \,.$$

For a free nickel(II) ion with equivalent 3d electrons or positrons, the

possible terms are ^3F, ^1D, ^3P, ^1G, and ^1S. The differences between these states are due to the electron repulsion terms in the Hamiltonian and they have been experimentally determined to be (35)

$$^1D \leftarrow {}^3F = 14.05 \text{ kK}$$

$$^3P \leftarrow {}^3F = 16.71 \text{ kK}$$

$$^1F \leftarrow {}^3F = 23.03 \text{ kK}$$

$$^1S \leftarrow {}^3F > 50 \text{ kK}$$

Usually ligand field calculations show improved agreement with experimental values if the free ion values are reduced. This is justified by allowing a small amount of covalent character which spreads out the atomic metal orbitals over the ligands. In our calculation, the reduction factor F is treated as a parameter.

If the spin is ignored, the nickel(II) ion has twenty-five states corresponding to above mentioned five energies. Maki (1) has derived the sets of twenty-five orthonormal linear combinations of products of pairs of atomic orbitals using the angular momentum lowering operation and the orthogonality relationships as outlined in Condon and Shortley (30). The S state was omitted since it has a free ion energy much higher than all others and its energy remains relatively unchanged in the ligand field.

In considering the effect of the ligand field a 24 x 24 matrix is obtained with each element of the form

$$H_{ij} = \langle \Psi_i (1,2) \mid V \mid \Psi_j (1,2) \rangle$$

where Ψ_i is the wave function of the free ion state. By imposing symmetry requirements and eliminating any interaction between singlet and triplet states, the matrix is factored into noninteracting blocks. In order to obtain the energy eigenvalues, numerical values for all the nonzero H_{ij}'s are needed. These integrals may be expressed as a sum of one electron integral's of the form for the ith electron

$$(h_{mm'})_i = \langle \underline{d}_{m_i} \mid V \mid \underline{d}_{m_i'} \rangle$$

Since the ligand field is of D_{4h} symmetry, the rule (24) that $m'-m = 0$ or ± 4 applies and many of the $(h_{mm'})_i$ are equal to zero. Maki (1) has simplified the 24 x 24 matrix using the above procedure and the final form modified for a ligand field calculation is given in Appendix I. The nonzero one electron integrals have been defined as follows:

$$(h_{22})_i = Q_2 = \langle \underline{d}_2 \mid V \mid \underline{d}_2 \rangle$$

$$(h_{11})_i = Q_1 = \langle \underline{d}_1 \mid V \mid \underline{d}_1 \rangle$$

$$(h_{00})_i = Q_0 = \langle \underline{d}_0 \mid V \mid \underline{d}_0 \rangle$$

$$(h_{2-2})_i = B_{2-2} = \langle \underline{d}_2 \mid V \mid \underline{d}_{-2} \rangle$$

The matrices have been evaluated with the aid of Burroughs B-5500 electronic computer at the Rich Electronic Computer Center and the final results

are shown in Figure 15 and 16.

One requirement that must be made is that the ground state must be a singlet state. Figure 15 reveals that the use of the free ion splitting (F=1) and the splitting of levels as determined for $[Cu(II)(DACO)_2]^{++}$ yields a triplet ground state with the $^1A_{1g}$ state 7.22 kK higher in energy. Using a value of P = 1.25 also yields a ^3E_g ground state with the $^1A_{1g}$ still 4.72 kK above. According to this trend a considerable increase in P would eventually produce a $^1A_{1g}$ ground state. A considerable increase in P would be equivalent to stating that the ligand field is much stronger for the nickel(II) complex. Since there is no reason for believing that it should be much stronger, increasing P to 1.6 or greater seems unreasonable. The effect of the reduction of the splitting of the free ion state is observed in Figure 16 where the value of the P is 1.25 and the value of F is varied. The $^1A_{1g}$ becomes the ground state at F = 0.60.

When considering the question of the validity of the calculation, the biggest cause for doubt involves the parameter F. The reduction in value of this parameter corresponds to admitting that there is covalent bonding. But, unfortunately, all of the d orbitals are assumed to be delocalized to the same extent. Since this is not a good assumption, the validity of the ligand field approach decreases proportionally to F. Bostrup and Jorgensen (36) have calculated F values of between 0.70 and 0.78 for octahedral amine complexes of nickel(II). If these values are used as a standard, the upper limit of 0.65 indicates that there is more than the usual room for error.

Another factor which should be considered is that of spin-orbit coupling.

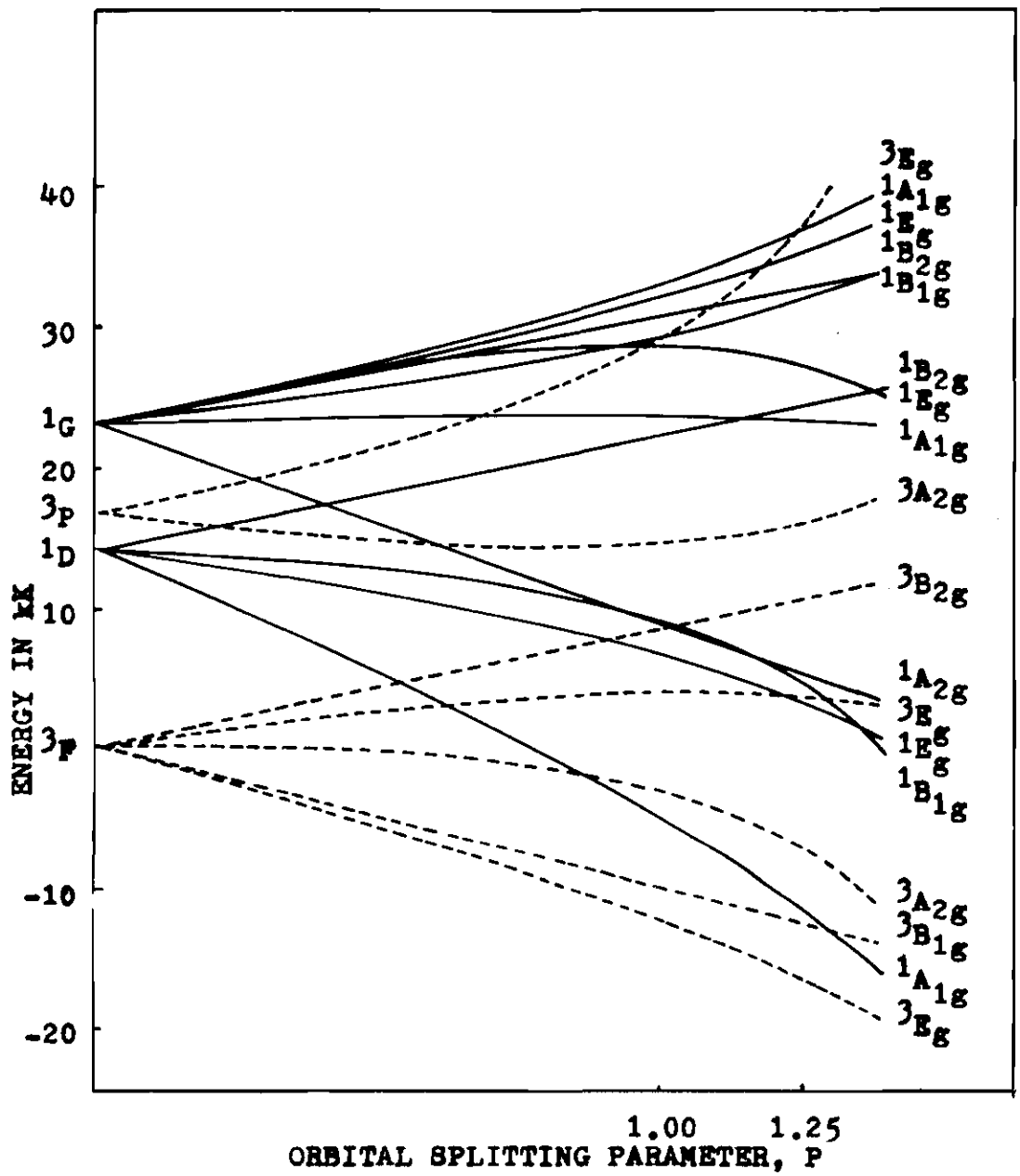

Figure 15. The Energy Level Diagram for Square-planar Complexes as a Function of the Orbital Splitting Parameter.

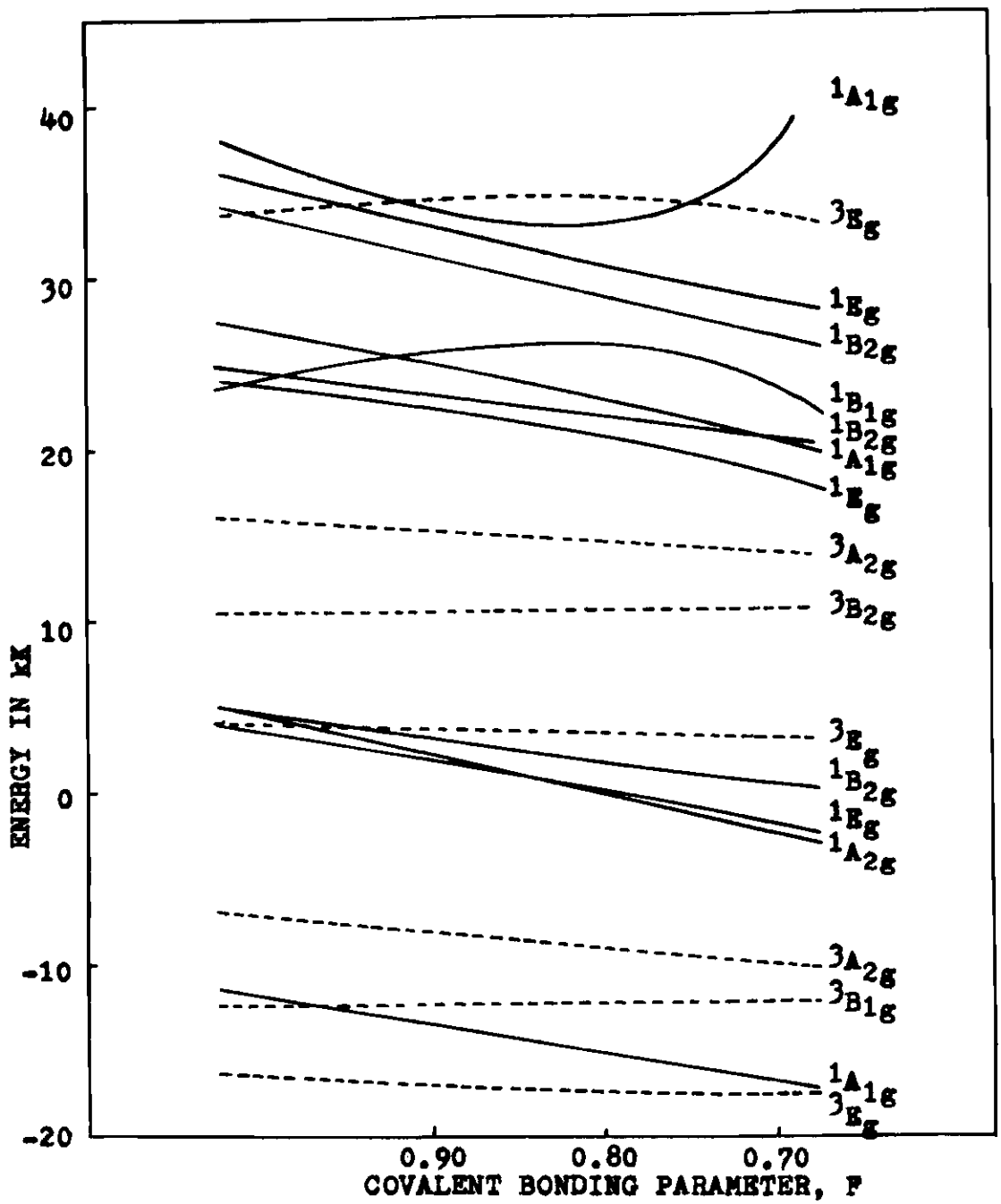

Figure 16. The Energy Level Diagram for Square-planar Complexes as a Function of the Covalent Bonding Parameter. (All energies are relative to the ^3F state of the free ion being zero energy. The splitting of the d orbitals is taken as 125% of the splitting in $[Cu(DACO)_2]^{++}$.)

If spin-orbit coupling is significant a calculation which includes this would produce a ground state of lower energy than one that ignores this fact. This stabilization is due to an interaction with higher triplet states and could be accounted for by the normal configuration interaction approach if the value of the spin-orbit coupling constant were known for the complex. Perhaps this value could be estimated from the experimentally known value (3) for the free ion just as the energy separation of terms used in the complex are related to the free ion. This would greatly complicate (37) the calculation because of the greater size and complexity of the matrices to be diagonalized.

Our calculations show that if the values of F is limited from 0.64 to 1.00 and P is from 1.00 to 1.25 no singlet to singlet $\underline{d}$ to $\underline{d}$ transitions occur in the region from 0 to 12 kK, three $\underline{d}$ to $\underline{d}$ singlet transitions may occur in the region from 12 to 24 kK, and finally no $\underline{d}$ to $\underline{d}$ singlet transitions occur in the region from 24 to 30 kK. No order of the $\underline{d}$ to $\underline{d}$ transitions in the region of 12 to 24 kK could be assigned because the levels are very close together and do change order over the range of values for the parameters.

We must admit that we could produce practically any energy diagram imaginable if we used as parameters W_1, W_2, W_3 and F. If we did this our calculation would degenerate into a curve fitting calculation and would hardly be worth the effort. Because we have used only F and P as parameters but have restricted them to values that are justified and within the framework of the calculations we are able to draw meaningful conclusions.

CHAPTER V

DISCUSSION AND CONCLUSIONS

All of the complexes except one that are considered in this study have been described as having square-planar ligand fields. The exception is $Ni(TAH)(ClO_4)_2$ which has never been described in the literature.

The chemical analysis of $Ni(TAH)(ClO_4)_2$ indicates that the given formulas represents the correct stoichiometry in the crystalline state. A comparison of the mull infrared spectra of the crystalline solid and the starting material of the preparation, $Ni(TAHD)(ClO_4)_2$, revealed that the product showed an additional N-H stretching absorbance at 3180 cm^{-1}, the loss of the C = N stretch absorbance at 1700 cm^{-1} and major differences in the C - C bending absorbance. The visible spectra of the mull revealed a broad absorption band with its maximum at 18.5 kK, while the DMSO solution revealed an equivalent absorbance with its maximum at 18.7 kK with an extinction coefficient of 254 $cm^{-1}m^{-1}1$. The magnetic data revealed a magnetic moment of 0.5 Bohr magnetons which is not what one expects from diamagnetic states, but what one usually observes for square-planar complexes of nickel(II). The spectral data indicate that we have succeeded in hydrogenating the square-planar $Ni(TAHD)(ClO_4)_2$ (16) to produce square-planar $Ni(TAH)(ClO_4)_2$.

In our magnetic moment studies we have found that moments for the square-planar bis(DACO) copper(II) perchlorate corresponds quite well to the spin only

value of 1.86 Bohr magnetons. In our studies as well as other studies of square-planar nickel(II) complexes (12, 15, 16) moments have been found to be between 0.55 and 0.40 Bohr magnetons. This high moment is usually attributed to temperature independent paramagnetism without worrying about the source of it.

The temperature independent character of the moment indicates that is is not due to a thermal population of an excited triplet state (38). Furthermore it is doubtful whether this high moment could be due to a certain percentage of nickel(II) ions having octahedral coordination (39) since the moments of all of the reported square-planar nickel(II) complexes fall in a narrow range. An interaction of some excited triplet states with the singlet ground state may be responsible for the moments.

This approach may be appreciated by examining the "weak field" approximation of ligand field theory in greater detail. In our calculation as well as Maki's (1) the assumption was made that the spin function may be separated from the orbital function. If this assumption is not made, ligand field arguments must be made on the splitting of J (total angular momentum) rather than L (orbital angular momentum). The results are that matrix elements similar to those in Appendix I are in groups based on the irreducible spin-space representations rather than just the space representations. These spin-space irreducible representations contain both singlet and triplet state elements (37) and the resulting energy levels reflect diagonalizing of the entire irreducible representation.

The matrix elements given in Appendix I can not be related to the ones using the total angular momentum because the total angular momentum matrices

are established using the double group symmetry requirements, but perhaps qualitative conclusions may be reached. The interaction of a triplet state with a singlet state will be in the form of a pertubation matrix in which the off diagonal elements are related to the spin-orbit coupling parameters. As in all perturbation matrices, the interaction of two states increase as the value of the off diagonal element increases and decreases as the difference in energy of the diagonal elements increase. This is shown in Figure 17. At points well away from X_1, the interaction is very small and the triplet state is essentially a pure triplet state. At point X_1, the two states become degenerate if the off diagonal element is zero. If it is not zero, the states are no longer degenerate, but represent a complete mixture of triplet and singlet states. As one moves away from X_1 to X_2 the amount of mixing decreases and the ground state becomes more like a true singlet state.

The magnetic studies indicate that the square-planar bis(DACO) nickel(II) perchlorate dihydrate has a weak temperature independent paramagnetism which is far below a spin only triplet value of 3.87 Bohr magnetons. Such a situation would be described by an energy level diagram which allows singlet-triplet interaction where the mainly singlet ground state is low enough so that there is not a temperature controlled population of the higher state.

The visible solution spectra of the nickel(II) square-planar complexes are shown in Figures 3 through 7. Generally, there was no change in the absorption bands indicative of any significant solvent-complex interaction. The only exception is the complex $Ni(TAH)(ClO_4)_2$. The aqueous solution spectra reveals a

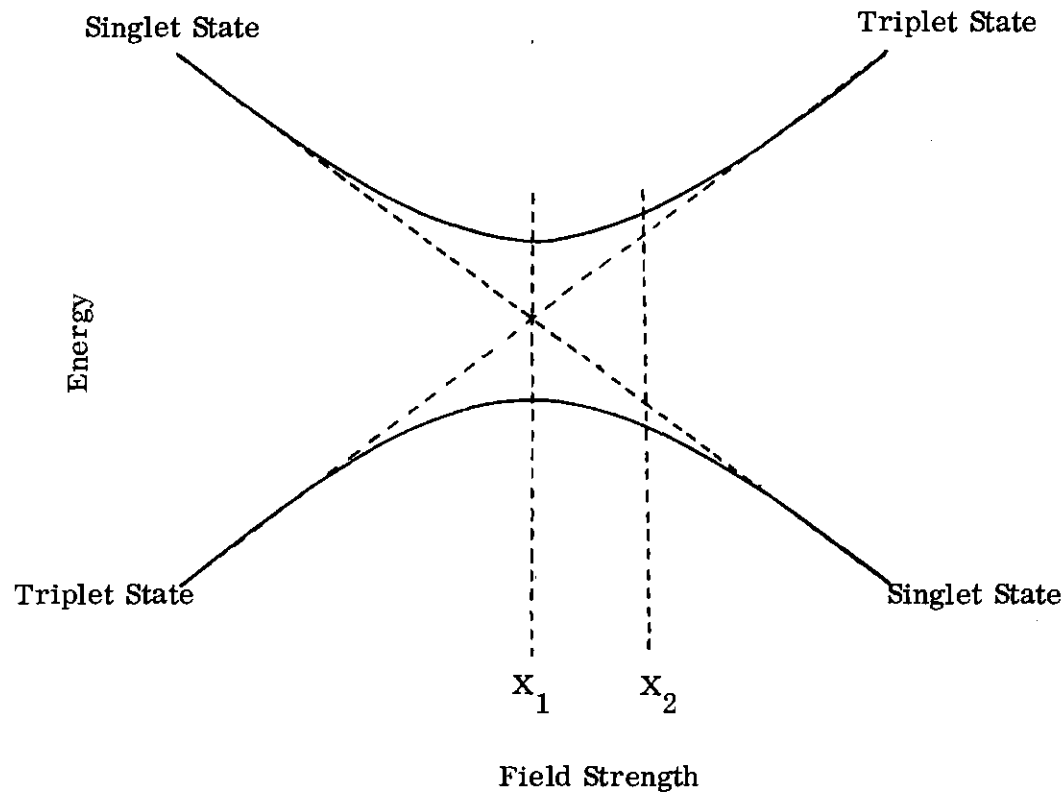

Figure 17. A Qualitative Illustration of Singlet-Triplet State Interaction.

(The broken line represents the pure states with no interaction. The curves represent the states with interaction.)

shoulder at 18.5 kK and a maximum at 22.0 kK with an extinction coefficient of about 100 units. The absorbance ratio of the shoulder and the maximum changed with temperature and produced an isosbestic point at 19.7 kK. The temperature dependence indicates that in aqueous solution there is an equilibrium between two forms, with the form having its maximum at 22.0 kK being more stable at higher temperatures. Both forms have spectra which are typical of square-planar complexes (that is, one maximum in the range between 25 and 15 kK). The form that

is the least stable at higher temperatures has its maximum at almost the same energy as that form in DMSO and solid state, while the other form which absorbs at a higher frequency is more like the other amine systems investigated.

An explanation of this may be that since the amines in $Ni(TAH)ClO_4)_2$ are secondary amines, a number of geometric arrangements of the carbon chains are possible and easily convertible in aqueous solutions due to proton exchange. Solvation in water as compared to DMSO may produce different interactions with the ligand systems and different stabilities of the geometric arrangements. The various geometric forms may have different ligand fields, and therefore, differences in spectral data are observed. The very much greater extinction coefficient of $Ni(TAH)(ClO_4)_2$ in DMSO may be due to a distortion from the essentially square-planar symmetry of the ligand field because of the very bulky ligand system so that the center of symmetry of the complex is lost. Noncentrosymmetric complexes are known to have higher extinction coefficients (24). The observation of this equilibrium and apparent distortion emphasizes the importance of keeping the ligand systems as simple as possible so that the interpretation of the spectra will be as simple as possible.

The square-planar amine complexes are yellow to maroon in color with one broad absorption band occurring in the visible region between 15 and 25 kK having an extinction coefficient of 50 to 260 1 cm^{-1} $mole^{-1}$. In the past, the common practice has been to assign this band to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition (40) and assume that the other d to d transitions occur at higher energies buried in the very intense charge transfer band. The assignment of the $^1A_{1g} \rightarrow {}^1A_{2g}$ is made

on the basis that the $^1A_{1g}$ is mostly $d_{x^2-y^2}$ orbital and that the $^1A_{2g}$ is mostly a combination of the $d_{x^2-y^2}$ and d_{xy} orbitals. These orbitals are the ones relatively unexposed and therefore they are the ones least strongly effected by the solvent interaction which should be mostly in the z direction.

The solution spectra revealed that the positions of the visible bands in the square-planar Ni(II) complexes are not measurably influenced by the solvent. The spectra of bis(DACO) nickel(II) perchlorate shown in Figure 3 reveals a featureless maximum at 22.4 kK with no absorption between 9 and 19 kK and between 27 and 37 kK. This indicates that either all three d to d transitions are within the broad band at 22.4 kK or that there are one or two absorptions in this peak with the second and/or third absorption being buried in the intense charge transfer band which has appreciable absorbance at frequencies greater than 37 kK. Square-planar complexes that have been investigated in the past (5, 23, 40) have always shown a very intense charge transfer band beginning at frequencies of approximately 30 kK. Because of the high frequency of the first charge transfer band, the spectra of the DACO complex is the first clear evidence that no d to d transitions occur in the range between 30 and 37 kK. If one or more of the d to d transitions of the DACO complex occur within the charge transfer band, the energy difference of the excited states must be at least 14 kK. Gaussian resolution shows that two or three transitions may be within the visible band, but this is not definitive evidence. The Gaussian resolution of the polarized spectra into three definite components would seem to be strong evidence that the broad visible absorption band of the square-planar amine complexes does in fact contain all three one electron d to

d transitions. The assignment of transitions is as follows:

$$^1A_{1g} \rightarrow {}^1E_g \quad 21.6\ kK$$

$$^1A_{1g} \rightarrow {}^1A_{2g} \quad 22.3\ kK$$

$$^1A_{1g} \rightarrow {}^1B_{1g} \quad 23.7\ kK$$

Further evidence comes from ligand field calculations. Even if the values of the parameters, F and P, are varied considerably, the excited states ^1E_g, $^1A_{2g}$ and $^1B_{1g}$ never differ greatly in energy. Furthermore, this same conclusion may be reached by an examination of the crystal field calculation of Maki (1). We may wonder why our ligand field calculation did not produce results in closer agreement with magnetic and spectral data. The answer is that our ligand field calculation, as all ligand field calculations, is only an approximation. Probably the biggest difficulty with this type of calculation, which is well known, is that the uniform reduction of all the electron-electron repulsion parameters is not really an adequate allowance for the effect of covalent bonding. For example, in the case at hand, the $d_{x^2-y^2}$ orbital should be the only d orbital which is significantly involved in covalent bond formation while the remainder of the d subshell orbitals should remain as essentially pure atomic d orbitals. Thus we really should have three different sets of repulsion parameters; one involving two electrons in the $d_{x^2-y^2}$ orbital, one involving one electron in the $d_{x^2-y^2}$ orbital and one in another d orbital, one involving two electrons in d orbitals other than the $d_{x^2-y^2}$ orbital

(this one would be reduced little if any from the free ion value). If we compare the polarized single crystal spectra and the calculated results, we see that an increase of 33 percent in the difference in energy between the calculated ground state and excited states is required before we have agreement with the largest splitting we have calculated. Certainly such values could be obtained if we varied F and P enough, but the new values required would be difficult to justify. So at best, we may conclude that the calculation is only an approximation to the energy levels, but it certainly gives clear evidence that the broad band observed for square-planar complexes contains all three d to d transitions.

Our magnetic data show that spin-orbit coupling and the resultant mixing of singlet and triplet states is important and should not be ignored. Complexes of the first transition series generally have relatively small values of the spin-orbit coupling constants and therefore it is doubtful if including this factor will improve the calculated spectra much.

The polarized single crystal spectra of bis(DACO)copper(II) perchlorate dihydrate indicates that the order of the energy levels is $^2B_{1g} < {}^2B_{2g} < {}^2E_g < {}^2A_{1g}$. This order has often been proposed on the basis of crystal field arguments, but has never been experimentally found. The spectral and electron spin resonance studies (41) of crystalline salts of bis-ethylenediaminecopper(II) salts indicate the order to be $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$. In these crystal structures the anion was found to be within distances ranging from 2.56 to 3.00 Å along the z axis of the complex. This indicates that there is considerable interaction and this was further demonstrated through the use of infrared spectra (41). The maximum of

the absorbance band of the perchlorate salt was found to be at 18.8 kK, while the maximum of the bis(DACO)copper(II) perchlorate dihydrate occurs at 20.7 kK. Because of the coordinating anion, a comparison to the DACO complex is expected to show that the $^2B_{1g} \leftarrow {}^2A_{1g}$ transition should occur at lower energy in the ethylenediamine complexes and this may be one of the reasons for the observed band occurring at lower frequency.

The polarized crystal spectra of pentaamminecupric ammonium perchlorate indicates the order $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$ (28). An assumption is made that the ammine at a distance of 3.75 Å along the z axis (42) is far enough away so that the copper(II) to ammine interaction may be ignored. If this is a good assumption, then the above order is in disagreement with our assignment. A study of the visible spectra of solvated copper(II) ions in anhydrous 2-picoline (43) indicates that interaction of anions at distances of 5 Å or more have considerable influence on the visible spectra, and so the assumption that the z direction interaction is negligible in the pentaamminecupric ammonium perchlorate structure seems questionable. Examination of models indicates that the DACO complex may have methyl groups or hydrogen at similar distances, but certainly the interaction of these atoms or groups will be less than with an ammonia dipole. Evidence that there is a fairly strong interaction in the pentaamminecupric ammonium perchlorate structure is displayed by a blue color typical of ammonical solutions of copper(II). These considerations indicate that the assumption that the z direction interaction is not significant is probably not correct and therefore there is no real disagreement with our interpretation.

We have made the assignment of the single crystal spectra of bis(DACO) copper(II) perchlorate dihydrate to be as follows:

$$^2B_{1g} \rightarrow {}^2B_{2g} \quad 18.2 \text{ kK}$$

$$^2B_{1g} \rightarrow {}^2E_g \quad 20.8 \text{ kK}$$

$$^2B_{1g} \rightarrow {}^2A_{1g} \quad 23.8 \text{ kK}$$

A comparison of this spectra with the solution spectrum shown in Figure 8 indicates that the maximum changes from 20.75 kK for the crystal to 20.10 kK for aqueous solution and to 18.95 kK for pyridine solutions. The differences indicate that interaction is occurring along the z axis. The shift then is probably due to the fact that the energy of the $^2A_{1g}$ level decreases with interaction, and the observed band shift actually only reflects differences of the $^2A_{1g}$ level. This is in accordance with the experimental evidence that the $^2A_{1g}$ level is extremely sensitive to axial interaction (41, 43). Because of this, it is difficult to make a general assignment of the energy levels.

We have made a clear assignment for the bis(DACO)nickel(II) complex, but as of yet, we have not related our assignment to other systems. All of the square-planar nickel(II) ammines investigated with the exception of $Ni(TAH)(Cl)_4)_2$ have an extinction coefficient of near 100 units and have nearly the same shaped band envelope with some variation of position. The variation in position is probably due to small differences in ligand field strength. Because of the strong resemblance,

major differences in components seems unlikely. We must admit though, that on the basis of shape we can not confidently assign the same order of energies of the component bands that occur in each complex. Requiring the same order would imply that differences in these ligand systems is so small that relative energies of the very closely spaced excited states are not altered. From Table 8, we see

Table 8. Visible Absorption Spectral Data for Square-Planar Complexes of Nickel(II) Diamines

	Solvent	max, kK	ε max	Reference
$Ni(II)(DACO)_2(ClO_4)_2$	Water	22.40	115	This work
	DMSO	22.40	115	This work
	CH_3CN	22.45	120	12
	CH_3NO_2	22.45	112	12
$NiCTA(ClO_4)_2$	Water	22.80	125	This work
$NiCTB(ClO_4)_2$	Water	22.80	112	This work
cis-$Ni(CTH)_2(ClO_4)_2$	Water	22.00	93	This work
trans-$Ni(CTH)_2(ClO_4)_2$	Water	21.80	101	This work

that even the $Ni(CTA)(ClO_4)_2$ solution spectra show little differences. The slightly higher energy of absorption could be attributed to a small interaction of the π^* orbital of C = N with the d_{xz} and d_{yz} orbitals so that there is a slight increase in energy of the observed band. If we can be sure that the fields can be described as D_{4h}

and that there are no differences in interactions in all of the $\underline{d}$ orbitals except the $\underline{d}_{x^2-y^2}$ orbital, it is likely that no difference in order of the states occurs from the order we have assigned to the crystal of the nickel(II) DACO complex. Since the solution spectra show no solvent shifts, it is unlikely that axial interaction will alter the order, but the π^* bonding effects may be great enough in Ni(CTA)-$(ClO_4)_2$ and Ni(CTB)$(ClO_4)_2$ so that the order may differ for these complexes.

A comparison of the solvent shifts of the nickel(II) and copper(II) DACO complexes reveals that there is a much greater solvent shift in the nickel(II) complexes. This difference could not be due to different steric blocking of the axial position. The difference is probably due to the fact that copper(II) is a one positron case while nickel(II) is a two positron case. In the copper(II) case, the energy of the states is determined by the interaction of the $\underline{d}$ orbitals with the ligands, while in the case of nickel(II) the energy of the states is determined by the interaction of the $\underline{d}$ orbitals with the ligands and the interaction of the positrons with each other. What this positron-positron repulsion does is to scramble the $\underline{d}$ orbitals into states that are no longer a product of two one-positron orbitals, but a linear combination of orbitals. This means that an interaction along the $\underline{z}$ axis in the case of nickel(II) will not be as observable because the interaction will be distributed over many levels rather than one as in the case of copper(II).

If we consider the ligand field calculation and the spectral data, it appears that the energy of the orbitals is determined by the σ interaction with the $\underline{d}_{x^2-y^2}$ orbital and some crystal field or electrostatic interaction with the other orbitals. The fact that the $b_{2g}(\underline{d}_{xy})$, $e_g(\underline{d}_{xz}, \underline{d}_{yz})$ and $a_{1g}(\underline{d}_{z^2})$ lie fairly close together and

in order expected from an electrostatic point of view is an argument for crystal field theory. The fact that the $b_{1g}(\underline{d}_{x^2-y^2})$ orbital is so greatly different from the other orbitals indicates that electrostatics is not a good approach. The best description is the nonbonding levels, $b_{1g}(\underline{d}_{x^2-y^2})$, $e_g(\underline{d}_{xz}, \underline{d}_{yz})$, and $a_{1g}(\underline{d}_{z^2})$ lying fairly close together with their order being determined by electrostatics, and an anti-bonding $b_{1g}(\underline{d}_{x^2-y^2})$ lying at least 18 kK above these levels.

APPENDIX I

MATRIX ELEMENTS

^1A_g

$$H_{11} = 2Q_2 + F(23.03)$$

$$H_{gg} = 2/35\ (Q_2 + 16Q_1 + 18Q_0) + F(23.03)$$

$$H_{5'5'} = 2/7\ (4Q_2 + Q_1 + 2Q_0) + F(14.05)$$

$$H_{19} = 2/(35)^{1/2}\ B_{2-2}$$

$$H_{15'} = 4/(7)^{1/2}\ B_{2-2}$$

$$H_{5'9} = 4/7(5)^{1/2}(Q_2 + 2Q_1 - 3Q_0)$$

$^1A_{2g}$

$$H_{22} = 2Q_2 + F(23.03)$$

$^1B_{1g}$

$$H_{55} = 1/7\ (3Q_2 + 8Q_1 + 3Q_0 + 3B_{2-2}) + F(23.03)$$

$$H_{1'1'} = 2/7\ (2Q_0 + 2Q_2 + 2B_{2-2} + 3Q_1) + F(14.05)$$

$$H_{5\,1'} = 2(3)^{1/2}/7(Q_0 + Q_2 + B_{2-2} - 2Q_1)$$

$^1B_{2g}$

$$H_{66} = 1/7\ (3Q_2 + 8Q_1 + 3Q_0 - 3B_{2-2}) + F(23.03)$$

$$H_{2'2'} = 2/7\ (2Q_0 + 2Q_2 - 2B_{2-2} + 3Q_1) + F(14.05)$$

$$H_{2'6} = 2(3)^{1/2}/7(Q_2 - 2Q, + Q_0 - B_{2-2})$$

^1E_g

$$H_{33} = Q_1 + Q_2 + F(23.03)$$

$$H_{77} = 1/7\ (Q_2 + 7Q_1 + 6Q_0) + F(23.03$$

$$H_{3'3'} = 1/7\ (6Q_2 + 7Q_1 + Q_0) + F(14.05)$$

$$H_{37} = (1/7)^{1/2}\ B_{2-2}$$

$$H_{33'} = (6/7)^{1/2} B_{2-2}$$

$$H_{73'} = (6)^{1/2}/7(Q_2 - Q_0)$$

$^3A_{2g}$

$$H_{77} = 2/5\ (Q_2 + 4Q_1)$$

$$H_{3'3'} = 2/5\ (Q_1 + 4Q_2) + F(16.71)$$

$$H_{3'7} = 4/5\ (Q_1 - Q_2)$$

$^3B_{1g}$

$$H_{44} = Q_0 + Q_2 + B_{2-2}$$

$^3B_{2g}$

$$H_{33} = Q_o + Q_2 - B_{2-2}$$

^3E_g

$$H_{11} = Q_1 + Q_2$$

$$H_{55} = 1/5\ (3Q_2 + 5Q_1 + 2Q_0)$$

$$H_{1'1'} = 1/5\ (3Q_0 + 5Q_1 + 2Q_2) + F(16.71)$$

$$H_{15} = -(3/5)^{1/2}\ B_{2-2}$$

$$H_{1'1} = 2/5\ B_{2-2}$$

$$H_{1'5} = (6/5)^{1/2}(Q_0 - Q_2)$$

APPENDIX II

The Computer Program for the Resolution of Spectral Data*

```
COMMENT THREE PEAK RESOLUTION;
BEGIN
     FILE IN VHS(2,10);
     FILE OUT PRNT 6(2,15);
     INTEGER NO,I,K,N;
     REAL DEL,SPHI,SS,RHO,DELTA,SPSI,THETA;
     REAL ARRAY A,W,X,Y(0:200),PHI,PSI(0:15);
     LABEL START, ONE, TWO, THREE;
     FORMAT FMT1(X5,I3,//);
     FORMAT FMT2(X5,3F15.6);
     FORMAT FMT3(//,X5,I4,3F15.7,//);
     FORMAT FMT4(//);
     FORMAT FMT5(X5,F15.7);
     FORMAT FMT6(///,X30,"PATTERN SEARCH FOR 3 GAUSSIAN",
          "CURVES");
     FORMAT FMT7(X10,"BASE POINT NUMBER",I4,X3,"STEPSIZE",
          F12.7,//);
     FORMAT FMT8(X5,9F8.4,X5,F12.4);
     FORMAT FMT9(/,X10,"EXPLORATORY MONE RESULTS",/,X5,
          9F8.4,X5,F11.4);
     FORMAT FMT10(//,"AFTER",I4,"BASE POINT EXPLORATIONS",
          "WE HAVE ATLEAST A LOCAL OPTIMUM LOCATED AT:",
          /,X5,9F8.4,X5,F8.4);
     FORMAT FMT11(X5,F15.7,X5,F15.7);
     FORMAT FMT12(8(X4,F9.3));
PROCEDURE INPUT;
     BEGIN
     READ(VHS,/,N);
     FOR I←1 STEP 1 UNTIL N DO
     BEGIN
     READ(VHS,/,W(I),A(I));
     Y(I)←A(I)/10;
     X(I)←10*5/W(I);
     END;
     READ(VHS,/,K,DEL,RHO,DELTA);
     FOR I←1 STEP 1 UNTIL K DO
     BEGIN
     READ(VHS,/,PSI(I));
     END;
```

* This algol program is a modified form of one written by W. W. Swart (44).

```
    IF SPHI<SS THEN SS←SPHI ELSE
    BEGIN
    BAM←2xDEL;
    PHI(I)←PHI(I)-BAM;
    SPHI←EVALUATE(PHI,X,Y,N,K);
    IF SPHI<SS THEN SS←SPHI ELSE PHI(I)←PHI(I)+DEL;
    END;
    END;
    END OF E;
WRITE(PRNT(NO));
INPUT;
NO←0;
WRITE(PRNT,FMT6);
WRITE(PRNT,FMT4);
START:SPSI←EVALUATE(PSI,X,Y,N,K);
ONE:SS<SPSI;
FOR I←1 STEP 1 UNTIL K DO
BEGIN
PHI(I)←PSI(I);
END;
NO←NO+1;
E;
COMMENT ARE EXPLORATORY MOVES SUCCESSFUL;
IF SS<SPSI THEN
BEGIN
THETA←PSI(I);
PSI(I)←PHI(I);
PSI(I)←2xPHI(I)-THETA;
END;
SPSI←SS;
SS←SPHI←EVALUATE(PHI,XY,N,K);
IF SS>SPSI THEN
BEGIN
GO TO THREE;
END;
COMMENT MAKE EXPLORATORY MOVES;
NO←NO+1;
E;
COMMENT IF SUCCESSFUL MAKE NEW PATTERN MOVE, OTHERWISE GO
    TO ONE AND TRY NEW EXPLORATORY MOVES;
IF SS<SPSI THEN GO TO TWO ELSE GO TO ONE;
END
ELSE
COMMENT IF EXPLORATORY MOVES WERE NOT SUCCESSFUL REDUCE
    STEP SIZE UNTIL THESE ARE LESS THAN DELTA;
THREE:  IF DEL≥DELTA THEN
BEGIN
DEL←RHOxDEL;
```

```
      CLOSE (VHS,RELEASE);
      WRITE(PRNT,FMT1,N);
      FOR I←1 STEP 1 UNTIL N DO
      BEGIN
      WRITE(PRNT,FMT2,X(I),W(I),Y(I));
      END;
      WRITE(PRNT,FMT3,K,DEL,RHO,DELTA);
      FOR I←1 STEP 1 UNTIL K DO
      BEGIN
      WRITE(PRNT,FMT5,PSI(I));
      END;
      END OF INPUT;
PROCEDURE CALCULATE;
      BEGIN
      REAL ARRAY E1,E2,E3,D,T(0:200);
      FOR I←1 STEP 1 UNTIL N DO
      BEGIN
      E1(I)←PHI(1)xEXP(-(PHI(2)-X(I))*2/PHI(3)*2);
      E2(I)←PHI(4)xEXP(-(PHI(5)-X(I))*2/PHI(6)*2);
      E3(I)←PHI(7)xEXP(-(PHI(8)-X(I))*2/PHI(9)*2);
      T(I)←E1(I)+E2(I)+E3(I);
      D(I)←T(I)-Y(I);
      WRITE(PRNT,FMT12,W(I),X(I),Y(I),E1(I),E2(I),E3(I),
          D(I),T(I));
      END;
      END OF CALCULATE;
REAL PROCEDURE EVALUATE(PHI,X,Y,N,K);
      REAL ARRAY PHI,X,Y(0);
      INTEGER K,N;
      BEGIN
      REAL SUM;
      INTEGER I;
      REAL ARRAY FX(0:200);
      SUM 0;
      FOR I←1 STEP 1 UNTIL N DO
      BEGIN
      FX(I)←PHI(1)xEXP(-(PHI(2)-X(I))*2/PHI(3)*2)+PHI(4)x
          EXP(-(PHI(5)-X(I))*2/PHI(6)*2)+PHI(7)xEXP(-(PHI(8)
          -X(I))*2/PHI(9)*2);
      SUM←SUM+(Y(I)-FX(I))*2;
      END;
      EVALUATE SUM;
      END OF EVALUATE;
PROCEDURE E;
      BEGIN
      REAL BAM;
      FOR I←1 STEP 1 UNTIL K DO
      BEGIN
      PHI(I)←PHI(I)+DEL;
      SPHI←EVALUATE(PHI,X,Y,N,K);
```

```
GO TO ONE;
END;
WRITE(PRNT,FMT10,NO,PHI(1),PHI(2),PHI(3),PHI(4),PHI(5),
    PHI(6),PHI(7),PHI(8),PHI(9),SS);
CALCULATE;
END.
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VITA

Vernon Schievelbein was born on June 4, 1943 in San Antonio, Texas, the son of Bernice and Gilbert Schievelbein. He attended East Central Rural High School and Schertz-Gibolo High School graduating from the latter in June, 1961. After attending San Antonio Junior College for two years, he entered Trinity University completing the requirements for a B. S. degree in Chemistry in August, 1965. He entered the Georgia Institute of Technology in September, 1965, and in June, 1969, the degree of Doctor of Philosophy in Chemistry is to be completed under the supervision of Dr. D. J. Royer.

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